Introduction to Quantum Mechanics for Electrical Engineers

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Foreword

For older engineers, like me, there is something disturbing and unsatisfying in the description of nature according to quantum mechanics. The picture, seen as a whole, is beautiful, impressive, fascinating, and powerful. And yet, because it all is based on a few startlingly unobvious and non-self-evident axioms, it bothers me.

There have been those who can use the picture in spite of all their misgivings, and contribute to it creatively as, for instance, Einstein did. Others are so impeded by their misgivings that they have difficulty in using quantum mechanics as a tool in their trade, even when it is obviously to their advantage to do so. I belong to the latter group.

Is that so because I did not learn it in school? I do use other techniques now which I did not learn in school. Yes, but they do not offend my intuition! Well, what about my intuition? It is not offended by the notion of electrons, neutrons, protons, etc., final and indivisible units of matter. After all, the ancient Greeks had already postulated atoms. It is offended by quantized orientations of spins in a magnetic field. It is offended by finite units of radiation. How wide is such a photon? How long? It depends on how it is measured, it is said. And to be sure, there exist perfectly consistent schemes which predict exactly and with unfailing success the results to be expected from a variety of measurements.

However, my intuition is unengaged, or disengaged, and consequently I am unhappy. Furthermore, other mental and spiritual resources are affected. Without the active cooperation of the intuitive faculty, the ability to visualize special and general relationships, the power to perceive differences and likenesses, analogies and contradictions, to make models and systems, the drive to invent and to create—all these are weakened, if not paralyzed altogether.

This is a serious matter for me as an engineer, whose profession consists in applying scientific research to progress and innovation in communications.

It is clear that my intuition needs to be improved. How can that best be accomplished? By getting thoroughly used to, and familiar with, the new concepts.

A sense of 'familiarity' will make acceptable any concept, however non-self-evident it may seem at first. By tying such a concept to one already known and accepted, by connecting it to an old picture, or to a model of

fewer dimensions, by resorting to simple extrapolations of well-understood relations—by such means 'familiarity' can be created. (I suppose I have just described one of the methods of teaching.)

Many books on quantum mechanics already exist, addressed to an audience with a wide spectrum of sophistication. Those books I happened to have read are addressed to physicists, or written by physicists. The process of 'familiarization' carried out in them is, with few exceptions, based on physical models and pictures, and uses the physicists' language. They do not talk in the engineers' language, nor do they attempt to use the engineers' models and pictures, except occasionally and then rather condescendingly.

It should be clear by now why, some time ago, I pleaded for an 'Introduction to Quantum Mechanics for Electrical Engineers'. Pure selfishness on my part, of course. But, rarely is pure selfishness not also of some benefit to others.

The others who will benefit from a book such as this are engineers, old ones as well as young ones, those who like myself did not learn quantum mechanics at school at all, or those who did but remained uneasy and unsatisfied about the basic assumptions of quantum mechanics; those who had difficulties in accepting the dogmas—beg your pardon—the axioms of quantum mechanics. If and when familiarity with the notions of quantum mechanics will have led to a liberation of the intuition and consequently to a flowering of creativity in engineers, I expect to see a reversal of a trend which has become apparent: namely, that the major inventions in the recent past in the sciences of communication and electronics have been made by physicists (who all presumably had quantum mechanics at school).

The aspiration of scientists is to discover. The aspiration of engineers is to invent. When scientists—physicists—took over more and more of the engineer's function of inventing they took most of the glory and the prestige with them. This is not good for the engineers. In the long run, this is not good for the scientists either, because science can only thrive in a flourishing environment of engineering. And vice versa, of course. Symbiosis, the most desirable state for science and engineering, requires that *both* be healthy and strong.

And so I heartily welcome this book.

Bell Telephone Laboratories Inc.   DR R. KOMPFNER
Holmdel, New Jersey

Preface

In this book, an attempt has been made to present quantum mechanics from the point of view of electrical engineers and to show that they are already familiar with many of the fundamental mathematical concepts and algebraic operations which are required. It is, therefore, hoped that on the one hand, electrical engineering departments may find the book useful in setting up introductory courses of quantum mechanics while, on the other hand, qualified engineers may use it to gain familiarity with the fundamental concepts involved.

This book frequently departs from the presentation common in introductory texts prepared for the use of physicists. The differences, however, are didactic, rather than of substance, with the obvious omission of some specialized topics. For brevity, the author has assumed throughout that the readers are quite familiar with the calculus, vectors, and, in some cases, matrices. In the author's opinion, the book presents the very minimum of material which is required for an understanding of the underlying principles which have found application in modern electronic devices such as transistors, tunnel diodes, masers, and lasers.

The first two chapters of the book respectively contain a brief description of the basic features of quantum mechanics and an outline of the experimental reasons for its existence, this preliminary discussion being carried out strictly in terms of general physical concepts without any recourse to algebra. The following chapter (chapter 3) is possibly the most important in the book since it introduces many fundamental ideas. We discuss in it the concept of matter waves, Schrödinger's wave equation, Heisenberg's uncertainty principle, operators, and commutators. Chapter 4 starts with the general idea of standing waves and then discusses, in some detail, particles bound in potential wells, the harmonic oscillator, the hydrogen atom, potential barriers, and angular momentum. Chapter 5 is largely concerned with the concept of degeneracy, composite states, and the general properties of eigenfunctions, whereas chapters 6 and 7 form a group, respectively dealing with time-independent and time-dependent perturbation problems. Here, considerable use is made, for didactic reasons, of analogues based on transmission line theory. Chapter 7 also contains a brief exposition of the basic concepts of state vectors and matrix mechanics. Systems comprising more than a single particle are discussed in chapter 8 which ends with a brief introduction

to Bose–Einstein and Fermi–Dirac statistics. The important concept of spin is discussed in chapter 9, the argument being based largely on Dirac's relativistic wave equation. Here, the use of matrices will not disturb the electrical engineer, although it is reasonable to suggest that chapter 9 and sections 7.5, 8.4, and 8.5, are somewhat more advanced in character. Finally, chapter 10 provides a brief introduction to the concept of energy bands in crystals, the exposition again being assisted by the use of a suitable electrical analogy which, in this case, takes the form of a periodically loaded transmission line. The six appendices deal with topics which stand apart from the rest of the book, i.e., relativity correction, Poisson brackets, probability, effective mass for two interacting particles, Boltzmann's statistics, and Dirac's bra and ket notation. The MKS system of units is used throughout.

It gives the author great pleasure to thank Dr R. Kompfner of Bell Telephone Laboratories Inc., New Jersey, U.S.A., for kindly suggesting the need for a book of this kind and Mr Alan Reddish of the Hirst Research Centre, The General Electric Company, Wembley, England, for his readiness, on numerous occasions, to give freely and generously of his time and advice. Thanks are also due to Miss Gwynne Jenkins for her forbearance in deciphering numerous emendations and preparing the manuscript in its final form.

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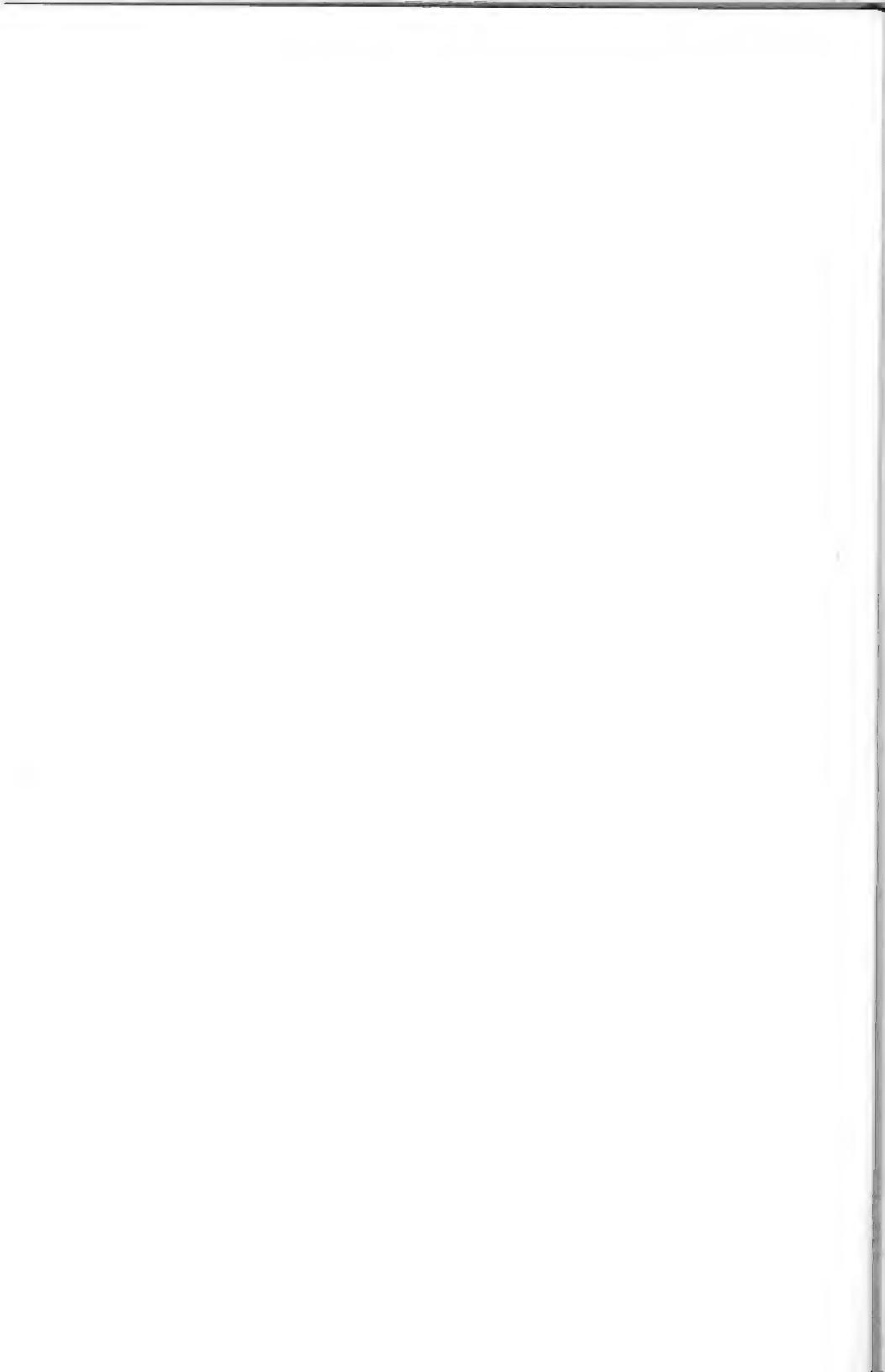
Contents

1. Introduction

In the course of the last decade, electrical engineers have seen a new link established between electronics and quantum mechanics. By now the stage has been reached when electrical engineers must become familiar with the fundamental ideas of quantum mechanics if they wish to understand the operation of such devices as transistors, tunnel diodes, masers, and lasers. In this new field of 'quantum electronics', the governing phenomena are on the atomic scale and are thus subject to quantum mechanical laws.

Furthermore, it is not always realized how familiar to the electrical engineer are the mathematical concepts used in quantum mechanics. This is particularly true in the wave-mechanical representation when the concept of waves, so basic to electrical engineering, is dominant. Although the physical significance of the waves is quite different in the two cases, the delicate mathematical apparatus involved is very similar and should be relatively familiar to electrical engineers. This similarity will be brought out as much as possible in the present volume.

It is usual to distinguish various different representations in quantum mechanics; for example, we have Schrödinger's *wave representation* based on his wave equation and Heisenberg's *matrix representation* based on the concept of observables, the two being embraced by Dirac's formulation in terms of state-space vectors. The choice of any given representation largely depends on the specific problem considered; similarly, the choice of coordinates in the solution of a differential equation is frequently governed only by the relevant boundary conditions. Since the elementary problems of quantum mechanics particularly lend themselves to the wave-mechanical representation, this is the representation usually adopted in this book, although, for the sake of completeness, other formulations will also be described very briefly.

Perhaps the most startling feature of the wave representation of quantum mechanics is the fact that a particle can no longer be adequately described by a mathematical mass point but must, instead, be associated with a *matter wave* which completely defines its dynamical state. Leaving aside the more philosophical implications of this wave–corpuscle duality, we can see that several important consequences of the new definition immediately follow.

First, since the Schrödinger equation defining the matter waves Ψ is a

wave equation, for many boundary conditions it can only be solved for certain values of its parameters called the *eigenvalues*, the corresponding solutions being called the *eigenfunctions*. In the case of an electron bound to the nucleus of a nonradiating atom this, as we shall see, leads quite naturally to the quantization of energy of the system, each energy *eigenstate* corresponding to one or more eigenvalues of the parameters for which the corresponding wave equation can be solved. It can be shown that other dynamical properties of particles or systems of particles, for example their linear and angular momenta, can be quantized.

Also we frequently find that when the energy of a particle is quantized, its position or linear momentum is not, the corresponding values following a continuous 'probability distribution' curve. Here we encounter another startling feature of quantum mechanics, namely its lack of support for strict determinism. Thus, if we wished to repeat many times the same simple experiment, such as the measurement of position of a particle, in general we could only predict, with the help of quantum mechanics, the frequency of occurrence of a given experimental result, never its actual value in any given case. It is true that we may be quite familiar with somewhat similar situations occurring in other branches of physics or engineering, for example in the kinetic theory of gases or in the study of traffic conditions in a telephone exchange, but in these cases it is always assumed that the probabilistic aspect of the problem is forced on us by the imperfection of our observations. Here for the first time, we encounter a more fundamental limitation—we are led to believe that it is basically impossible to obtain a more accurate, i.e., a more deterministic picture of nature than that provided by quantum mechanics, however good our instruments of observation. Thus, according to Heisenberg's 'uncertainty principle' any system under observation always exhibits an element of inherent unpredictability as well as quantization. This situation is closely related to the fact that every observation, however delicate, must, by necessity, affect the system. Even a casual glance at a polished metal cube requires some interaction between the beam of light reaching our eye and the cube, before any information about the cube can be conveyed to us at all. For massive objects the effect of such an interaction can be disregarded or, at worst, allowed for exactly, according to the rules of classical physics. In the case of atomic particles, however, this is no longer possible. Because of quantization there is a limit to the size of the smallest possible disturbance caused by the observation and, furthermore, the interaction has an element of uncontrollability. The object and the observer no longer remain separate but are inescapably coupled together by the mere act of observation to form a more complicated, compound system.[1,2]

Furthermore, the mere fact that a particle frequently must be represented by a composite wave called a 'wave packet' may bring to mind the

following result from telecommunication theory: a wave packet (or pulse), whatever its physical character, can be described either in the frequency or the time domain. When the packet is sharp in the frequency domain, it must be diffuse in the time domain and vice versa. This simple fact acquires singular importance in wave mechanics and is closely related to Heisenberg's uncertainty principle. For example, we shall see that various pairs of quantities, such as the energy and time, or the linear momentum and position of a particle, stand in a relationship which is similar to that of the frequency and time of an electromagnetic pulse. Although in quantum mechanics the physical significance of this *complementarity* is quite profound and does not depend for its existence on the particular choice of the wave representation, it may help us to remember that, mathematically at least, it follows directly from the introduction of the wave concept.

Finally, there is one more comment to be made which is often helpful in considering quantum mechanics for the first time—it concerns the relationship between geometrical and physical optics on the one hand and classical and quantum mechanics on the other.[3] It is well known that many problems in the study of light can be solved with the help of 'geometrical' optics, where light is assumed to follow straight or gently curving paths. Reflection, refraction, and the simple theory of optical instruments are all examples of the large measure of success which can be achieved by a judicious use of geometrical optics. This situation persists as long as the detail of the object which interacts with the beam of light, for example a simple aperture, is many times larger than the corresponding wavelength. Once this condition ceases to be satisfied, one begins to notice those phenomena which are intimately associated with the wave-like nature of light, for example interference and diffraction. In the case of the shadow of a simple aperture these phenomena may give rise to a lack of definition, a complicated fringe pattern beginning to appear in place of a sharp edge. Broadly speaking, light can be used successfully for investigating the shape and position of objects, until they become comparable in size to the light wavelength, a situation which constitutes the well known practical limit to the resolving power of an optical microscope. Somewhat similar considerations apply to classical and quantum mechanics, although the realization that this was in fact the case had to wait till the beginning of the present century. Briefly, as long as the objects under observation are large in comparison with the wavelength of the corresponding matter waves, one can safely use the laws of classical mechanics, which, in this context, correspond to the laws of geometrical optics. (Note, for example, the parallel between the law of least action in mechanics and the corresponding law of shortest light path in optics.[4]) However, once we come down to atomic distances or masses, the wave nature of particles becomes noticeable and leads to

interference and diffraction phenomena similar to those encountered in physical optics. Then one can no longer hope to describe the properties of a particle with an accuracy which is greater than that permitted by the 'grain' or wave-like pattern associated with it. Just as in the case of physical optics this approach leads to a much richer and at the same time more complicated description of nature; in the case of atomic particles such a description becomes quite indispensable. However, this approach makes the physical content of wave mechanics appear somewhat strange to all who are perhaps more familiar with the simple, but at the same time more approximate, approach of classical mechanics. Just as the laws of physical optics merge into those of geometrical optics when the necessary conditions are satisfied, so the laws of quantum mechanics follow the *Correspondence Principle* and smoothly transform into those of classical mechanics, where appropriate. One can say, in general, that the laws of quantum mechanics do not negate those of classical mechanics but extend them and thus refine our comprehension of nature.

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2. Outline of Experimental Evidence

In the previous chapter we have tried to describe, very briefly, the main features of quantum mechanics. It may be natural for the reader to ask why it is at all necessary to abandon classical mechanics and to introduce new concepts which are admittedly neither simple nor self-evident. As usual, the reasons for this are largely, though not exclusively, experimental in nature.

To put the matter briefly, at the turn of the century it was realized by some physicists that classical laws fail to explain the results of certain well defined experiments largely concerned with the interaction of electromagnetic radiation and matter. This situation made it necessary to re-examine the basic assumptions of existing theory and led to the development of quantum mechanics as we know it today. Naturally, many such experiments will be described in some detail later in this book to illustrate various applications of the new theory, but some are so persuasive that they may well serve as examples of the difficulties encountered in classical physics and are therefore outlined here.

Let us consider first of all a common observation in spectroscopy: emission (or absorption) spectra of atoms and molecules generally contain discrete lines. Figure 2.1 shows, for example, part of the emission spectrum (Balmer series) of atomic hydrogen. The discrete lines of such a spectrum provide simple evidence for some kind of 'quantization'; naturally, one would like to go further and predict the wavelengths of individual lines from a knowledge of the general properties of the atoms.
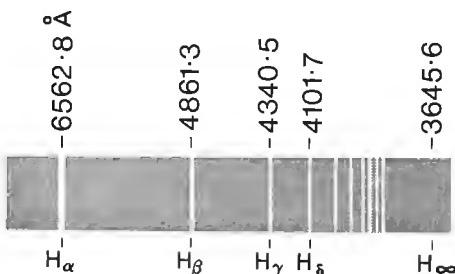
Fig. 2.1. Part of the emission spectrum of atomic hydrogen (Balmer series).

Indeed, it was shown by Schrödinger that this can be done by solving an appropriate differential wave equation which bears his name[1] (see also chapter 4).

Next, let us consider a problem posed by Rayleigh and Jeans[2,3] which is concerned with the inability of classical physics to explain the energy distribution of black-body radiation shown in Fig. 2.2. Consider a model
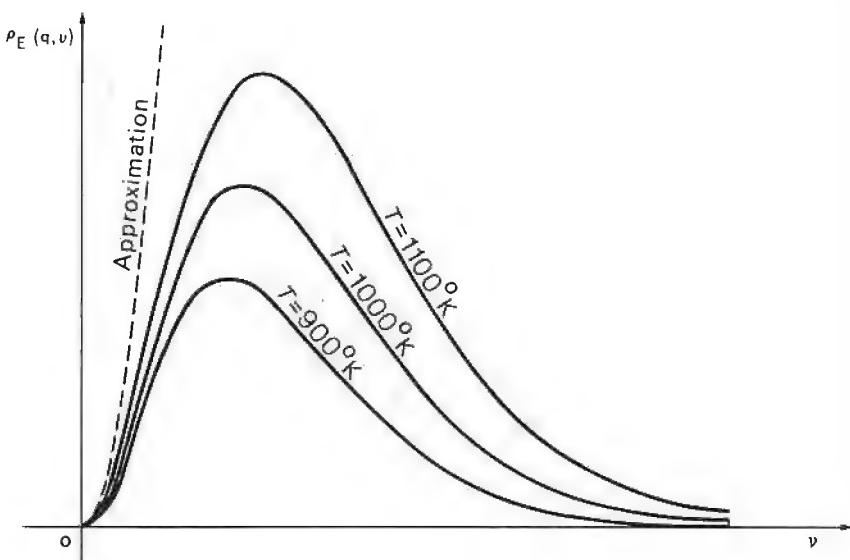
Fig. 2.2. Energy density of black-body radiation as a function of frequency.

of a black-body in the form of a metal container kept at a constant temperature. After a brief period of time, the interior of the container will be filled with electromagnetic radiation at many frequencies corresponding to the usual spectrum of resonant modes. The density of modes per unit frequency interval is given by the electromagnetic wave equation with the appropriate boundary conditions, as indicated in chapters 4 and 8. Since, in general, the mode density increases with frequency and since, in classical mechanics, there is no reason why energy should be unevenly divided among different modes, we reach the preposterous conclusion that the modes, being infinite in number, can accommodate an infinite amount of energy, the energy density steadily increasing with frequency, a state of affairs which is sometimes referred to as the 'ultraviolet catastrophe'. This is clearly contradicted by all experimental evidence, the black-body radiation having a well defined maximum beyond which it asymptotically approaches zero. In order to resolve this contradiction Planck[4] assumed that the interaction between electromagnetic radiation and matter must be quantized, the quantum of energy being proportional

to the frequency of radiation. Thus, the higher the frequency the larger the corresponding quantum of energy required for interaction—since such a process is assumed to take place at a fixed temperature characterizing the mean internal energy of the material enclosure, then above a certain energy value fewer and fewer larger quanta would be available for the interaction process. In this manner, Planck's assumption directly leads to an energy distribution which, beyond a certain point, asymptotically tends to zero with frequency. At the time the idea of quantization of energy was quite revolutionary and its significance may not have been clear even to Planck himself, but nevertheless, as we shall see later, the idea provided an important foundation for the subsequent development of quantum mechanics.

The next step in the same direction was taken by Einstein[5] who, backed by his own theoretical considerations and the available results of photoelectric experiments, further strengthened the arguments in favour of the quantization of radiation and energy. Einstein well knew that although the magnitude of the photoemission current depended on the intensity of incident light, the maximum energy of the emitted electrons did not, being a function of frequency alone. This could not be explained classically and could only mean that, for a given frequency, each emitted electron absorbed the same amount (or quantum) of energy, the rate of emission increasing with the intensity of light, i.e., the rate of arrival of the corresponding quanta of radiation (photons). The difficulties were further increased by the fact that the photoemission process seemed to be virtually instantaneous ($< 10^{-9}$ sec), the time delay being quite independent of the intensity of incident radiation. If electromagnetic radiation were assumed to be uniformly distributed in space, as would be required by classical theory, the amount of energy available for interaction over the volume of a single atom would be lower by several orders of magnitude than required, unless the interaction process were allowed to continue for days or even months, contrary to the experimental evidence. Again, the only logical explanation appeared to be provided by the quantization process proposed by Einstein. Thus, in spite of the well-established wave nature of light clearly in evidence in interference, scattering, and polarization experiments, there were certain situations when light energy was strongly quantized, the photoemission process being one of them. The concept of quantization of the electromagnetic field not only provided an explanation for the puzzling experimental facts relating to photoemission, but, in view of the implied wave–particle duality, also stimulated further theoretical inquiries and substantially contributed to the development of modern quantum mechanics.

Lastly, let us consider, very briefly, two more experiments which clearly indicate the wave-like character of particles and thus complete the symmetry of properties possessed by electromagnetic radiation and

matter. Although the experiments were performed after the fundamental theoretical papers of de Broglie[6] and Schrödinger[1] had been written and were specifically designed to test the validity of their theories, they should be mentioned here since they are both simple and convincing. Davisson and Germer,[7] remembering Bragg's experiments on X-ray diffraction by a crystal lattice and accepting the fact that, according to a formula introduced by de Broglie, 54 eV electrons would have a wavelength comparable to that of soft X-rays (1·67 Å), directed a univelocity electron beam at the surface of a crystal of nickel. Immediately a strong interference pattern appeared, Fig. 2.3, giving rise to pronounced peaks in certain directions, well in agreement with Bragg's formula (see section 3.2).
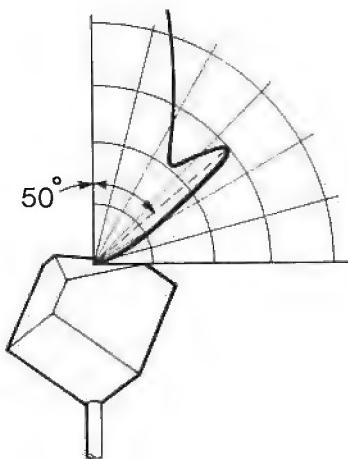
Fig. 2.3. Diffraction pattern produced by reflection of a beam of electrons from nickel.

At about the same time Thomson and Reid[8] decided to repeat X-ray diffraction experiments with powdered crystals but, this time, using a high voltage (13–64 kV) electron beam for irradiating 300–500 Å thick films of gold, aluminium, and celluloid. Again they obtained clearly identifiable diffraction rings, Fig. 2.4, which were in close agreement with Bragg's formula and the postulated de Broglie wavelength of the electrons (see section 3.2). These experiments seemed to confirm beyond reasonable doubt that the wave–particle duality applied not only to electromagnetic radiation but also to matter, and that it could be a fundamental feature of physical phenomena. At the time the impact of many similar experiments, together with the vast amount of spectroscopic evidence available, materially assisted in the acceptance of quantum mechanics as a valid and surprisingly accurate description of nature.
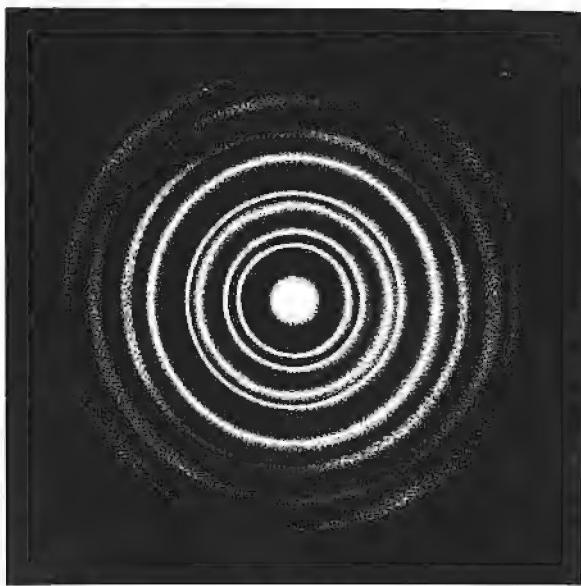
Fig. 2.4. Diffraction pattern produced by passing a beam of electrons through a gold foil.

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3. General Principles of Quantum Mechanics

We have seen in the first two chapters how the work of Planck,[1] Einstein,[2] de Broglie,[3] and Schrödinger[4] led to the quantization of electromagnetic radiation and the introduction of the concept of matter waves. These two ideas, when taken together, strongly suggested the inherent wave–particle duality of both radiation and matter and thus laid the foundations for many concepts of modern physics. In this chapter we will discuss, more fully, the matter waves and their governing Schrödinger equation, including some of the consequences, both experimental and theoretical, of the wave-mechanical representation of nature.

3.1. Basic facts about waves

Since we shall be concerned with the wave representation of quantum mechanics, it will first be useful to review some familiar facts about wave propagation. Consider a wave of amplitude F travelling in the z-direction, where F, for example, may represent voltage or current along a transmission line or a single component of a plane electromagnetic wave in vacuum. The appropriate one-dimensional wave equation is then

$$\frac{\partial^2 F}{\partial z^2} = \frac{1}{v_{\mathrm{p}}^2}\frac{\partial^2 F}{\partial t^2} \tag{3.1}$$

The general solution of this equation is

$$F = g\left(t - \frac{z}{v_{\mathrm{p}}}\right) + h\left(t + \frac{z}{v_{\mathrm{p}}}\right) \tag{3.2}$$

where g and h are arbitrary functions of the argument. This can be easily verified by substitution in (3.1).

One particularly simple solution of (3.1) is

$$F = A\,\mathrm{e}^{-j\omega(t - z/v_{\mathrm{p}})} = A\,\mathrm{e}^{-j(\omega t - \beta z)} \tag{3.3}$$

where ω is the *angular frequency* and β is the *phase constant* (i.e., the imaginary part of the *propagation constant* $\gamma = \alpha + j\beta$). An exponential rather than a trigonometric form is shown here, because exponentials are easier to manipulate, even though in most cases the actual physical

quantity would vary sinusoidally and would thus be given by the real or imaginary part of (3.3). (Electrical engineers usually employ $\exp\{j(\omega t - \beta z)\}$ rather than $\exp\{-j(\omega t - \beta z)\}$ which is more common in wave mechanics.)

In the above solution all points of the wave travel with the same *phase velocity* v_p and thus the shape of the wave does not change with time. Such a wave can be characterized by a single angular frequency ω (or frequency $\nu = \omega/2\pi$), a single phase velocity v_p and a single phase constant

$$\beta = \frac{\omega}{v_p} \tag{3.4}$$

It also has a unique *wavelength* given by

$$\lambda = \frac{v_p}{\nu} = \frac{2\pi v_p}{\omega} = \frac{2\pi}{\beta} \tag{3.5}$$

A more general solution of (3.1), when the wave is more complicated than a simple sine or cosine function, cannot be specified just by a single pair of (ω, v_p) or (ω, β). This is fairly obvious from the fact that, in order to represent an arbitrarily shaped periodic function with the help of Fourier series, we require an infinite number of sinusoidal or monochromatic wave trains. The shape of such a composite wave is no longer preserved in time, unless, by a happy coincidence the phase velocity v_p given by (3.4), i.e., the ratio of ω to β remains the same for all constituent waves. However, this is an exceptional situation, the medium then being called 'non-dispersive'. For 'dispersive' media which are much more common in practice, the phase velocity v_p (or the phase constant β) becomes a function of ω, this dependence being often expressed in terms of the so-called ω–β diagram, a representation which is particularly familiar to microwave engineers. Figure 3.1 shows an ω–β diagram for arbitrary dispersion; it is clear from the drawing that the slope of a straight line connecting an arbitrary point on the curve with the origin gives the corresponding phase velocity $v_p = \omega/\beta$.
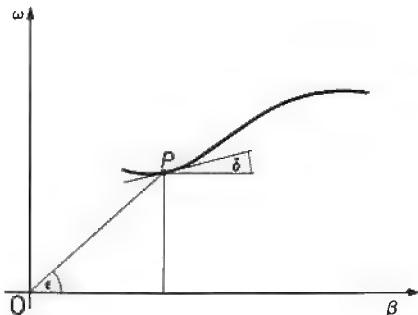
Fig. 3.1. An arbitrary dispersion curve.

Since in a dispersive medium the constituent wave trains travel with different phase velocities, a new quantity, the velocity of the composite wave itself, becomes of importance. However, since the shape of the composite wave is continuously changing, this velocity, i.e., the *group velocity* v_g, can be readily visualized over short distances only.

Consider two component wave trains which differ respectively in phase velocity and wavelength by dv_p and $d\lambda$, as shown in Fig. 3.2. The time it takes for the maximum of the 'group' at P_1 to fall back by λ to P_2 is, from Fig. 3.2, $d\lambda/dv_p$, so that the velocity of the group relative to the wave
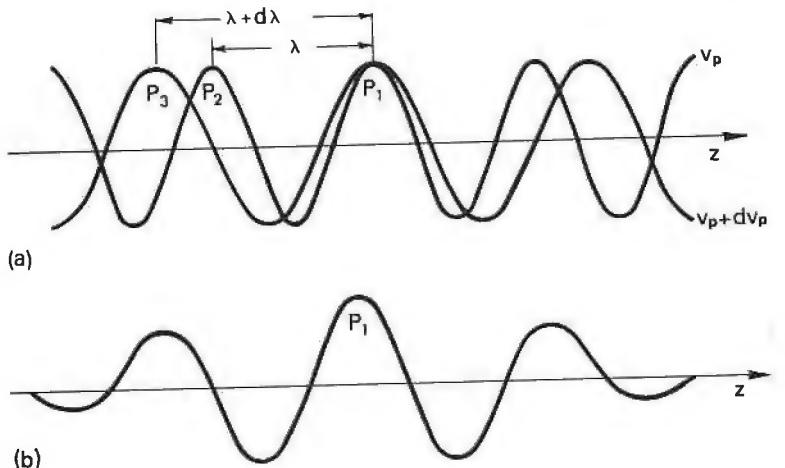
Fig. 3.2. A composite wave consisting of two wave trains respectively differing in phase velocity and wavelength by dv_p and $d\lambda$.

train is $-\lambda\, dv_p/d\lambda$. If we now subtract this quantity from the phase velocity v_p we obtain the group velocity v_g relative to the stationary laboratory frame of reference

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda}$$

$$= v_p - \lambda\left(v + \lambda \frac{dv}{d\lambda}\right)$$

$$= -\lambda^2 \frac{dv}{d\lambda}$$

$$= -\lambda^2 \frac{dv}{d\beta}\frac{d\beta}{d\lambda}$$

$$= \frac{d\omega}{d\beta} \tag{3.6}$$

where we have used (3.5) in the second and fifth lines. We can see from (3.6) that the group velocity can be defined as the instantaneous velocity of a small number of wave trains $d\beta = 2\pi \, d(1/\lambda)$ extending over a frequency range $d\nu = d\omega/2\pi$. In non-dispersive media $v_p = v_g$ by (3.6) and from (3.4) the corresponding ω–β curve is a straight line through the origin. For an arbitrary dispersion curve shown in Fig. 3.1, $v_g = \tan \delta$ is quite different from $v_p = \tan \varepsilon$. (Note that the group velocity becomes zero for maxima and minima of the ω–β curve.)

There is one particular type of composite wave which will be important to us in our further discussion—it is the so-called 'wave packet'. We may think of a wave packet as being produced by the superposition of an infinite number of monochromatic wave trains of different frequencies. The overall effect is to generate at a given instant of time constructive interference in a certain region of space and complete destructive interference anywhere else. It can be shown[5] that the region of constructive interference and hence the wave packet itself travels with the group velocity v_g. Thus, recapitulating, in a non-dispersive medium, $v_p = v_g$ and the shape of the wave packet does not change with time. Examples are a radar pulse travelling through free space, and a voltage or current pulse propagating along a loss-less transmission line. In a dispersive medium, the shape of the wave packet changes with time. An example is the propagation of a voltage pulse along a dispersive delay line, as used in pulse compression radar.

3.2. Waves in quantum mechanics

So far we have been discussing features of wave propagation which are probably familiar to most readers. We will now try to explain the manner in which the concept of waves is made use of in quantum mechanics. A striking feature of the matter waves Ψ used in the wave representation of quantum mechanics is the fact that they exhibit strong dispersion. For a free particle this dispersion is given by

$$v_p = \tfrac{1}{2}v_g \tag{3.7}$$

and is brought about by the following physical reasoning. Anticipating the fact that in quantum mechanics we may have to deal more often with wave packets rather than monochromatic waves, we will attach physical significance to the group velocity v_g in preference to the phase velocity v_p; assuming that a wave packet represents in quantum mechanics a point particle, we identify the group velocity v_g with the particle velocity v. The expression for the kinetic energy of a free particle moving with velocity v is given by

$$E = \tfrac{1}{2}mv^2 = \tfrac{1}{2}mv_g^2 = \tfrac{1}{2}m\left(\frac{d\omega}{d\beta}\right)^2 \tag{3.8}$$

Let us now accept Einstein's interpretation of the experimental evidence from photoemission that the radiation energy is quantized[2] and extend this principle to matter waves in general by writing

$$E = h\nu = \frac{h\omega}{2\pi} = \hbar\omega \qquad (3.9)$$

where h is Planck's constant and $\hbar = h/2\pi$. When taken together, (3.8) and (3.9) put a constraint on the Ψ-waves forcing a nonlinear dependence of β on ω; thus the phase velocity of the individual Ψ-waves comprising a wave packet cannot remain constant but must depend on ν (or ω). From (3.8) and (3.9) we obtain

$$\hbar\omega = \tfrac{1}{2}m\left(\frac{d\omega}{d\beta}\right)^2 \qquad (3.10)$$

which, after integration, gives us

$$\beta^2 = \frac{2m\omega}{\hbar} \qquad (3.11)$$

so that, substituting from (3.4), we get

$$v_{\mathrm{p}} = \frac{\hbar\beta}{2m} = \left(\frac{\hbar\omega}{2m}\right)^{\frac{1}{2}} \qquad (3.12)$$

The corresponding ω–β diagram is shown in Fig. 3.3, the curve being a simple parabola with its apex at the origin. From (3.11) and (3.12), or from the definition of a parabola, we find that the required relationship between v_{p} and v_{g} is satisfied everywhere.

$$v_{\mathrm{g}} = \frac{d\omega}{d\beta} = \frac{\hbar\beta}{m} = 2v_{\mathrm{p}} \qquad (3.7a)$$
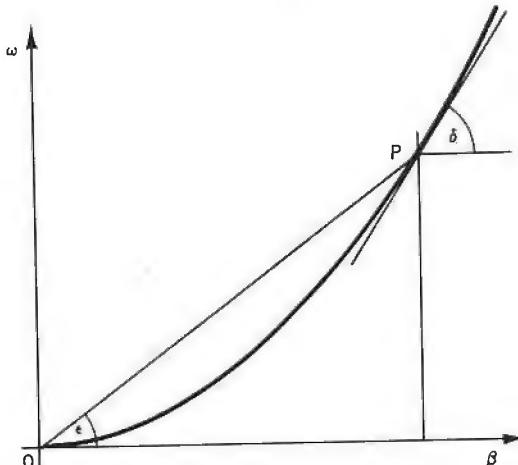
Fig. 3.3. The $\omega = (\hbar/2m)\beta^2$ dispersion curve.

Thus, the wavelength associated with a free particle travelling at velocity v, or the mean wavelength of the wave packet, is given by

$$\lambda = \frac{2\pi}{\beta} = \frac{h}{mv_\text{g}} = \frac{h}{mv} = \frac{h}{p} \tag{3.5a}$$

or

$$p = \hbar\beta \tag{3.13}$$

p being the linear momentum of the particle. This simple relationship between the wavelength λ and the momentum mv was first suggested by de Broglie[3] and then confirmed, in a manner already indicated in chapter 2, by numerous experiments, the most important of them being those of Davisson and Germer,[6] Reid and Thomson,[7] Kikuchi,[8] and Rupp.[9] Davisson and Germer, for example, directed a 54 eV beam of electrons on a clean surface of a crystal of nickel, as shown in Fig. 3.4.
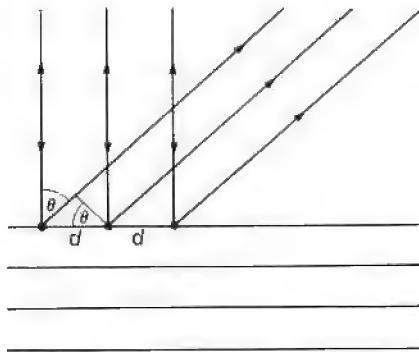
Fig. 3.4. Bragg reflection from atoms lying in the same plane.

According to (3.5a) the wavelength λ associated with 54 eV electrons is given by

$$\lambda = \frac{h}{mv} = \frac{h}{(2evmV)^{\frac{1}{2}}} = 12{\cdot}27 \times 10^{-10} V^{-\frac{1}{2}}$$

$$= 1{\cdot}67 \text{ Å} \tag{3.5b}$$

which corresponds to the soft X-ray region of the electromagnetic spectrum. If the electrons behave in a manner similar to X-rays, they should reinforce at an angle given by

$$n\lambda = d \sin \theta \tag{3.14}$$

which, for a spacing $d=2{\cdot}15$ Å is given, for $n=1$, by $\sin \theta = 0{\cdot}777$ or $\theta = 51°$. The experiment showed that in fact they did, the measured angle being 50°, Fig. 2.3, in very good agreement with the predicted value.

Similarly, Reid and Thomson shot 13 keV ($\lambda = 0.107$ Å) electrons through 300 Å thick films of aluminium, gold, and celluloid, getting diffraction rings identical to those obtained with X-rays of the same wavelength, as shown in Fig. 2.4. Since the electrons now had enough power to penetrate the material, the reinforcement was taking place from adjacent atomic planes belonging to randomly oriented crystals, so that now

$$n\lambda = 2d \sin \theta \qquad (3.15)$$

d being the separation between the planes, as shown in Fig. 3.5. We thus obtain for the diameter of the first bright ring

$$D = 4\theta L = \frac{2n\lambda L}{d} \qquad (3.16)$$

The measured values were again in close agreement with those predicted theoretically. In order to generalize the results even further Rupp[10]
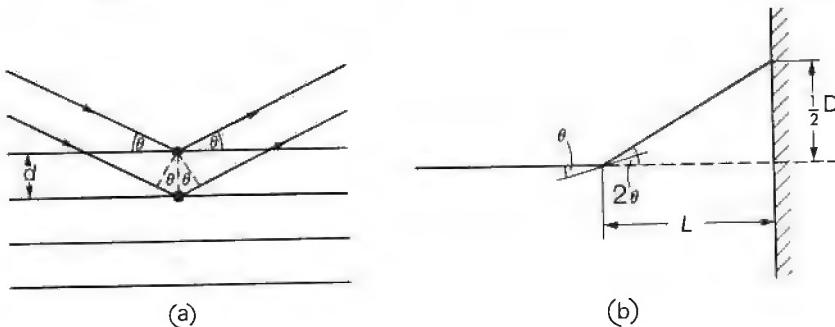
Fig. 3.5. Bragg reflection from atoms lying in different planes. (a) Schematic, (b) Actual layout.

obtained electron diffraction using a ruled grating in place of the atoms of a crystal and, a few years later, Estermann, Frisch, and Stern[11] performed somewhat similar experiments using helium molecules instead of electrons.

Finally, let us consider a particle which is subjected to a field of force defined by the potential energy V, where any change in the function $V = V(z)$ within a de Broglie wavelength is small compared to the kinetic energy of the particle,[12, 13] that is,

$$\lambda \left| \frac{\partial V}{\partial z} \right| \ll E - V \qquad (3.17)$$

Here E is the total energy of the particle given by

$$E = \tfrac{1}{2}mv^2 + V \qquad (3.8v)$$

the first term on the right-hand side of the equation representing the kinetic energy. (In electrical engineering it is customary to use V (or ϕ) for the electric potential function and qV for the electric potential energy, where q is the electric charge.) Inequality (3.17) expresses a condition comparable to that required for the validity of geometrical optics, i.e., that the index of refraction n should change only slowly with position.

Let us now derive the equivalent of (3.11). Using (3.8v) in place of (3.8) we obtain from (3.9) an equivalent of (3.10); after integration this equation yields

$$\omega = \frac{\hbar\beta^2}{2m} + \frac{V}{\hbar} \tag{3.11v}$$

The corresponding dispersion curve (ω–β diagram) is again a parabola similar to that shown in Fig. 3.3, except that now it cuts the vertical axis not at the origin but at the point $V/\hbar$. Although for any given β the phase velocity $v_p = \omega/\beta$ now differs from that for $V = 0$, the physically significant group velocity $v_g = d\omega/d\beta$ is still the same, being equal to the particle velocity v as before. It should be noted however that now both p and β, as well as V, are functions of z in general.

3.3. Matter waves and their physical meaning

At this point we should pause and inquire into the nature of the matter waves. We are quite familiar with the concept of an electromagnetic field associated, let us say with a charged particle, and the way this concept can be usefully applied in electrical engineering. The situation is some-what similar in the case of a particle of matter, and its associated field of matter waves. However, it has been already pointed out in chapter 1, that as long as the size of the particle is large compared with atomic dimensions, the classical approach is quite adequate and the existence of the field of matter waves can be ignored. Yet, as the relevant dimensions decrease and become comparable to those of an atom, we are forced to refine our approach and to assume the existence of a wave-like field which is associated with the particle and completely determines its dynamic state.

At first it was not at all clear what direct physical meaning could be attached to the matter waves function Ψ especially since, as a solution of Schrödinger's equation, it is in general complex. It was Born[14] who showed that direct physical meaning should be associated with the square of the amplitude $\Psi^*\Psi$ rather than with Ψ itself. If the matter waves are normalized by putting

$$\int_{-\infty}^{\infty} \Psi^*(z)\Psi(z)\,dz = 1 \tag{3.18}$$

or, in three dimensions

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r})\Psi(\mathbf{r})\ d\mathbf{r} = 1 \qquad (3.18)$$

where $d\mathbf{r}=dx\ dy\ dz$ is an element of volume, then, according to Born, $\Psi^*\Psi\ d\mathbf{r}$ gives the probability of finding the particle associated with the wave Ψ in the element of volume $d\mathbf{r}$ centred on $\mathbf{r}$. Thus, in general, the quantity $\Psi^*\Psi$ is a probability density function (see appendix 3)—it must always be real, positive, and less than one, the integrals (3.18) or **(3.18)** expressing certainty that the particle must exist somewhere in the space under consideration. The normalization procedure is only legitimate because the matter waves are required to satisfy the principle of super-position, which is implicit in the existence of interference phenomena. In this case the amplitude of each component of the wave packet can be reduced proportionately and the whole packet can be made to satisfy **(3.18)** without any accompanying change of shape. This is as far as we can go in attaching to Ψ-waves any physical significance which is meaningful in the macroscopic world.

The acceptance of **(3.18)** has two important consequences. We know from the theory of electromagnetic, acoustic or other waves that the square of the amplitude of a wave is closely related to power and that an integral of the type shown in **(3.18)** gives the total amount of power carried by the wave and thus must be finite. In practice, no travelling waves of infinite duration or infinite amplitude can exist in nature and whenever power calculations are involved we must somehow limit the ideal wave trains of mathematical analysis and turn them into wave packets. The same, in general, applies to Ψ-waves although here the requirement of a finite extent of the wave is associated with normalization and the concept of probability rather than power. In consequence, the Ψ-waves have the following property in common with all other waves encountered in physics—the amplitude should be finite everywhere and it should tend to zero at infinity sufficiently fast. (In mathematics, functions satisfying **(3.18)** are called *square integrable*.) Ordinary sine or cosine waves could never satisfy these conditions; thus in order to state that a particle merely exists somewhere between $-\infty$ and $+\infty$ we must already introduce the concept of a wave packet. This will, in itself, cause a slight spread in the amplitude and frequency of the wave. Alternatively, in cases when there are no apparent limits for the containment of the particle, i.e., in the case of the so-called free particle, we have to introduce some artificial limits of integration to make certain that the integral in **(3.18)** converges. It is usual in such cases to assume that the particle is confined to a 'box' which is sufficiently large to have a negligible effect on the properties of the corresponding Ψ-wave. Since in practice no really free particles can exist, quantum mechanics again forces us to acknowledge

the natural physical limitations of any system, even if it is only a 'thought' experiment.

The other point implied by (**3.18**) and Born's interpretation of $\Psi^*\Psi$ as a probability density function is the inherently statistical character of many predictions in quantum mechanics. For example, in the case of the simple electron diffraction experiments described in chapter 2, one can say that if the electron velocity is v, then the corresponding diffraction pattern is identical to that generated by a wave train of wavelength λ, where λ is given by (3.5a). However, in no circumstances can we predict what happens to an individual electron, apart from saying that it has a greater chance of landing on the brighter rather than the darker part of the screen, this much information being contained in the original probability density function $\Psi^*\Psi$. The electron diffraction experiments thus conveniently reveal the type of 'indeterminacy' which is very characteristic of quantum mechanics, something which has already been pointed out in chapter 1. It is also worth noting that an electron diffraction experiment can be easily altered to reveal the corpuscular rather than the wave-like character of the electrons. If in place of the photographic plate in Fig. 2.4 we put a large collection of scintillation counters, then the arrival of each individual electron will be registered as a separate event in the form of a light signal. Only when integrated over a period of time, for example, with the help of another photographic plate, would such events again reveal the wave-like character of the electrons, by showing that some scintillation counters arranged along concentric circles have been struck by electrons more often than others.

3.4. Schrödinger's wave equation

In the preceding section we have tried to show that in the wave-mechanical representation of quantum mechanics it is necessary to associate a wave packet with a free particle. In one dimension such a wave packet can be represented by a Fourier integral

$$\Psi(z, t) = (2\pi)^{-\frac{1}{2}} \int A(\beta)\, e^{-j(\omega t - \beta z)}\, d\beta \qquad (3.19)^*$$

where both the amplitude $A(\beta)/(2\pi)^{\frac{1}{2}}$ and the angular frequency $\omega(\beta)$ are functions of the phase constant β, the matter waves being, in general, highly dispersive, as is shown, for example, in (3.11) and Fig. 3.3.

Since the particle is free, we must have $V =$ const. or, as a special case $V = 0$. Let us now differentiate the wave packet (3.19) partially with

---

* Whenever no limits of integration are explicitly shown in this book it is implied that they are $(-\infty, +\infty)$.

respect to t; with the help of (3.11v) this leads to

$$jh \frac{\partial \Psi}{\partial t} = \frac{\hbar}{(2\pi)^{\frac{1}{2}}} \int \omega A \, e^{-j(\omega t - \beta z)} \, d\beta$$

$$= \frac{\hbar^2}{2m(2\pi)^{\frac{1}{2}}} \int \beta^2 A \, e^{-j(\omega t - \beta z)} \, d\beta + V\Psi \qquad (3.20)$$

ω and β being now independent of either z or t.

Similarly, differentiating (3.19) twice partially with respect to z we get

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial z^2} = \frac{\hbar^2}{2m(2\pi)^{\frac{1}{2}}} \int \beta^2 A \, e^{-j(\omega t - \beta z)} \, d\beta \qquad (3.21)$$

Substituting (3.21) in (3.20) we now obtain

$$jh \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial z^2} + V\Psi \qquad (3.22)$$

which is the celebrated Schrödinger equation of wave mechanics.[4] Since some coefficients in this equation are imaginary, its solutions must be expected to be complex in general. Although the above derivation of the Schrödinger equation has been carried out for the special case of $V = \text{const.}$, remarkably enough the equation can still be used for all V, even when V varies with z quite rapidly, or is a function of both z and t. The only real justification for Schrödinger's equation is, of course, the fact that, when applied, for example, to a hydrogen atom, it predicts the position of various lines of the emission spectrum with amazing accuracy. Without this and other experimental evidence the above derivation would not be very meaningful. It should be noted that (3.22), i.e., the *time-dependent* Schrödinger equation is, in fact, a 'diffusion' not a 'wave' equation, the time derivative being of the first and not of the second order, but the name 'wave equation' is too well established by now to be altered. The first-order dependence is significant because in this case a solution of the equation can be obtained with a knowledge of Ψ at one point in time only; thus, knowing, say, $\Psi(0)$ we can find from Schrödinger's equation $\Psi(t)$ for all other values of t. Otherwise, the usual laws of classical mechanics which, as we shall see in section 3.8, are still valid in quantum mechanics, but in a statistical sense, could no longer apply. Of course we can derive a wave equation of the usual form (3.1) from (3.19) by differentiating it twice with respect to time, but that equation is of no great significance since it contains the parameters of motion (E or p) and thus is not sufficiently general. It was Schrödinger's great achievement to recognize that the unusual first-order equation is of greater physical relevance and to show that its application and validity are quite general.

It should be added that an equation similar to (3.22) can be derived for

a function Ψ^* which is the complex conjugate of Ψ. Carrying out the necessary substitutions as in (3.20) and (3.21) we obtain

$$-j\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial z^2} + V\Psi^* \tag{3.23}$$

which differs from (3.22) only in the sign of its first term. The two equations (3.22) and (3.23) are equivalent in all respects so that all the available physical information concerning the associated particle is conveyed either by one or the other.

So far, for simplicity, we have considered one-dimensional motion only and assumed the linear momentum to be a scalar quantity, as indicated in (3.13). The argument, however, can be extended quite easily to three dimensions. In place of (3.13) we now write

$$\mathbf{p} = \hbar\mathbf{k} \tag{3.13}$$

where $\mathbf{k}$ is the propagation vector and has the same direction as the momentum and phase velocity vectors of the wave with which it is associated. (In view of (3.13) it would have been more logical to write $\boldsymbol{\beta}$ for $\mathbf{k}$ in (3.13), but $\mathbf{k}$ is too well established in wave mechanics to change it here.) In three dimensions the wave packet (3.19) assumes the form

$$\Psi(\mathbf{r}, t) = (2\pi)^{-\frac{3}{2}} \int A(\mathbf{k}) \, e^{-j(\omega t - \mathbf{r} \cdot \mathbf{k})} \, d\mathbf{k} \tag{3.19}$$

where $\mathbf{r}$ is the position vector of the particle and $d\mathbf{k} = dk_x \, dk_y \, dk_z$. Using (3.19) and following the approach which led to (3.22) and (3.23) we now obtain the three-dimensional form of the time-dependent Schrödinger equation

$$j\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(\mathbf{r}, t)\Psi \tag{3.22}$$

and its complex conjugate

$$-j\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V(\mathbf{r}, t)\Psi^* \tag{3.23}$$

where the possible dependence of the potential energy V on time has been indicated explicitly.

All comments referring to (3.22) equally apply to (3.22). In particular, one should remember that the solutions, i.e., the matter waves Ψ are, in general, complex quantities and thus they are easier to visualize as computational expedients rather than physical entities. The historical development of wave mechanics supports this point of view, since the mathematical formulation of the Ψ-waves[4] was arrived at prior to, and with less difficulty than, the corresponding explanation of their physical significance.[14] As we have already mentioned in section 3.3, it appears

that the only physical meaning which can be attached to Ψ-waves applies to the product $\Psi^*\Psi$ which represents a probability density function.

3.5. Heisenberg's uncertainty principle

In electrical engineering we are familiar with the reciprocal relationship that exists between the width of a pulse and the range of frequencies which are required for its composition.[15] If we take, for example, the rectangular pulse shown in Fig. 3.6a, then its Fourier transform is given by

$$F(v) = \int f(t)\, e^{-j2\pi vt}\, dt$$

$$= \int_{-\frac{1}{2}\Delta t}^{+\frac{1}{2}\Delta t} A\, e^{-j\omega t}\, dt$$

$$= A\, \Delta t\, \frac{\sin \frac{1}{2}\omega\, \Delta t}{\frac{1}{2}\omega\, \Delta t} \tag{3.24}$$

The frequency spectrum function $F(v)$ of the pulse is shown in Fig. 3.6b. Although the frequencies required for a faithful reproduction of the pulse
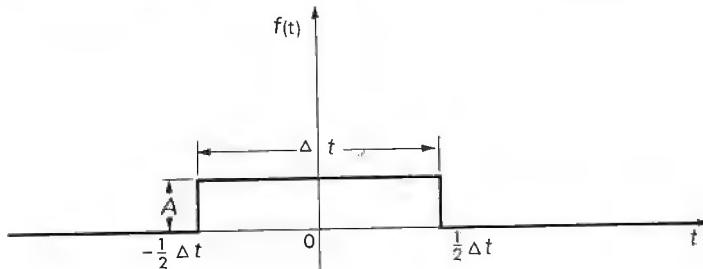
(a)
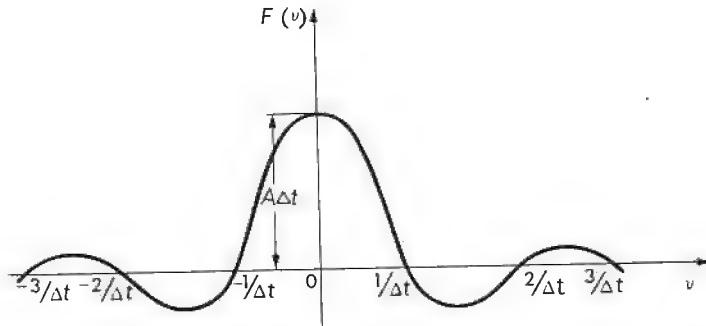
(b)

Fig. 3.6. (a) Single pulse of height A and duration Δt; (b) Frequency spectrum of a single pulse of height A and duration Δt.

in theory extend from $-\infty$ to $+\infty$, in a practical communication channel we would be satisfied with the result obtained by transmitting the main lobe of the spectrum. For that we require a bandwidth $\Delta v = 1/\Delta t$, as shown in Fig. 3.6b. We hence obtain the important relationship

$$\Delta v \, \Delta t = 1 \qquad (3.25)$$

This equation, together with Fig. 3.6 tells us that, for example, the bandwidth of a video amplifier necessary to reproduce a given pulse is inversely proportional to that pulse's width—the narrower the pulse the wider the bandwidth, and vice versa. In the limit a pulse of infinite duration, $\Delta t \to \infty$, would require zero bandwidth for its transmission. Similarly, a pulse of zero duration, $\Delta t \to 0$, would require an infinite bandwidth even to accommodate the main lobe. This reciprocal relationship between two such variables is quite general whenever we have to deal with finite as opposed to infinite wave trains or pulses. (If, for example, instead of a pulse we had a monochromatic wave of frequency v_0 and extending from $-\frac{1}{2}\Delta t$ to $+\frac{1}{2}\Delta t$, the corresponding frequency spectrum would be centred on v_0, but in other respects would be similar to that shown in Fig. 3.6b; the bandwidth now required for passing the main lobe would extend from $v_0 - 1/\Delta t$ to $v_0 + 1/\Delta t$ leading to $\Delta v \, \Delta t = 2$.)

As we shall see shortly, somewhat similar reasoning can be applied to the pulses or wave packets formed by the Ψ-waves, as was first shown by Heisenberg.[16] It should be added, however, that in quantum mechanics the philosophical consequences of this seemingly simple relationship between pairs of variables referring to the same wave packet are very profound indeed.

Let us now consider more closely the element of uncertainty which is inherent in the wave packet representation of a particle. It is fairly obvious that, because of its nonzero size, a wave packet cannot represent perfectly a point particle, although in the limit it can be made to approach zero by an infinite extension of the range of propagation vectors. Thus, in view of (3.19) or (**3.19**), we expect to find a situation somewhat similar to that in the above example.

Let us therefore examine (3.19) and its Fourier transform at $t = 0$, choosing the one-dimensional case first for simplicity.

$$\Psi(z, 0) = (2\pi)^{-\frac{1}{2}} \int A(\beta) \, e^{j\beta z} \, d\beta \qquad (3.26)$$

$$A(\beta) = (2\pi)^{-\frac{1}{2}} \int \Psi(z, 0) \, e^{-j\beta z} \, dz \qquad (3.27)$$

Figure 3.7 shows schematically the reciprocal relationship which exists between the two functions so that whenever we make $\Psi(z, 0)$ narrow,
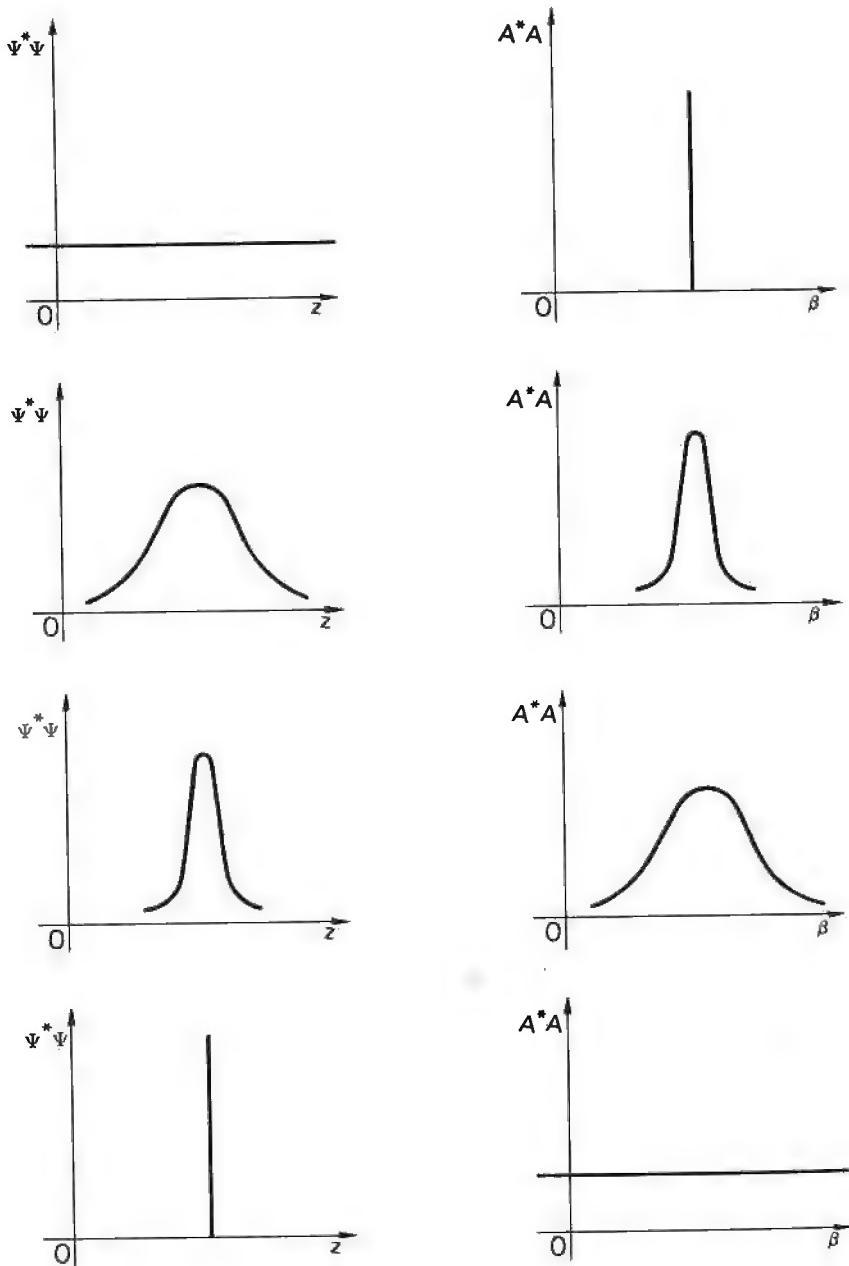
Fig. 3.7. Fourier integral pairs Ψ and A illustrating reciprocal spreading.

$A(\beta)$ spreads out and vice versa. Since

$$\int A^*(\beta)A(\beta)\,\mathrm{d}\beta = \int \Psi^*(z, 0)\Psi(z, 0)\,\mathrm{d}z = 1 \qquad (3.28)$$

where we have substituted in the first integral for $A(\beta)$ from (3.27) and then reversed the order of integration, it can be shown that A^*A is again a probability density function so that $A^*A\,\mathrm{d}\beta$ gives the probability of finding the phase constant within the interval $\mathrm{d}\beta$ centred on β. From (3.13) this is equal to the probability that the particle has its linear momentum within the range $\mathrm{d}p$ centred on p.

In deriving (3.25) we have used the length of the pulse for Δt and the half-width of the main lobe of the frequency spectrum function $F(\nu)$ as a suitable measure for the required bandwidth of the communication channel $\Delta\nu$. In general, it is more convenient to take the quantity called 'standard deviation' as a measure of the spread of the functions forming a Fourier pair. (This definition is particularly convenient when one of the functions follows a gaussian distribution, since then the other function of the pair is also gaussian.) A standard deviation is simply the square root of the mean square deviation from the average value; for example, if $\langle z \rangle$ is the average position corresponding to a given distribution defined by a probability density function such as $\Psi^*\Psi$, then $(z - \langle z \rangle)$ represents a deviation from such a position, the mean square deviation being the mean or average value of $(z - \langle z \rangle)^2$. Defining Δz and $\Delta\beta$ in this general fashion we obtain

$$\Delta z = \left\{ \int \Psi^*(z - \langle z \rangle)^2 \Psi \,\mathrm{d}z \right\}^{\frac{1}{2}} \qquad (3.29)$$

$$\Delta\beta = \left\{ \int A^*(\beta - \langle \beta \rangle)^2 A \,\mathrm{d}\beta \right\}^{\frac{1}{2}} \qquad (3.30)$$

where $\Psi^*\Psi$ and A^*A are the two probability density functions.

We can now derive a general expression for the minimum value of the product $\Delta z\,\Delta\beta$ using a form of Schwarz inequality first suggested in this context by Weyl and Pauli[17] and then further adapted to the discussion of uncertainty by Gabor.[18] Introducing new variables

$$z' = z - \langle z \rangle, \quad \mathrm{d}z' = \mathrm{d}z \qquad (3.31)$$

$$\beta' = \beta - \langle \beta \rangle, \quad \mathrm{d}\beta' = \mathrm{d}\beta \qquad (3.32)$$

to simplify the algebra, we obtain in place of (3.29) and (3.30)

$$\Delta z = \left\{ \int \Psi'^* z'^2 \Psi' \,\mathrm{d}z' \right\}^{\frac{1}{2}} \qquad (3.33)$$

$$\Delta\beta = \left\{ \int A'^* \beta'^2 A' \,\mathrm{d}\beta' \right\}^{\frac{1}{2}} \qquad (3.34)$$

where from (3.26) and (3.27)

$$\Psi'(z') = \Psi(z)\, e^{-j\langle\beta\rangle z'} \tag{3.35}$$

$$A'(\beta') = A(\beta)\, e^{j(\beta' + \langle\beta\rangle)\langle z\rangle} \tag{3.36}$$

the two functions $\Psi'(z')$ and $A'(\beta')$ again forming a Fourier pair. Bearing in mind that, in general,

$$\int A^*\beta^2 A\, d\beta = -\int \Psi^* \frac{d^2\Psi}{dz^2}\, dz = \int \frac{d\Psi^*}{dz}\frac{d\Psi}{dz}\, dz \tag{3.37}$$

whether the variables are primed or not, we obtain by substituting (3.37) in (3.34)

$$\Delta z\, \Delta\beta = \left\{ \int \Psi'^* z'^2 \Psi'\, dz' \int \frac{d\Psi'^*}{dz'}\frac{d\Psi'}{dz'}\, dz' \right\}^{\frac{1}{2}} \geqslant \frac{1}{2} \tag{3.38}$$

the last statement being in accordance with the Schwarz inequality. Multiplying both sides of (3.38) by $\hbar$, we obtain from (3.13)

$$\Delta z\, \Delta p \geqslant \tfrac{1}{2}\hbar \tag{3.39}$$

For simplicity we have so far restricted the uncertainty considerations to one-dimensional systems. However, if instead of using (3.19) we formed a Fourier pair similar to (3.26), (3.27) but based on (**3.19**), we would have obtained in place of (3.39)

$$\Delta x\, \Delta p_x \geqslant \tfrac{1}{2}\hbar$$
$$\Delta y\, \Delta p_y \geqslant \tfrac{1}{2}\hbar \tag{3.39}$$
$$\Delta z\, \Delta p_z \geqslant \tfrac{1}{2}\hbar$$

These are the well-known Heisenberg uncertainty relations for simultaneous observation of the position and momentum of a particle.

It might be of interest at this point to consider the consequences of (3.39) in connection with a simple experiment. Take a beam of particles which is arranged to pass through a slit, as shown in Fig. 3.8, the purpose
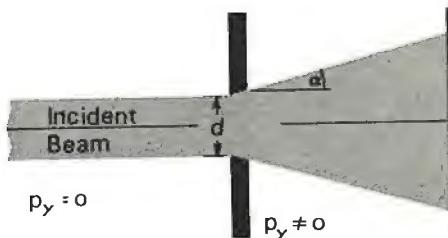

Fig. 3.8. Diffraction of a beam of particles by the edge of a slit.

of the slit being to localize the beam in the y-direction to within d, i.e., the uncertainty $\Delta y = d$. However, due to the wave character of matter the particles will suffer diffraction at the edges of the slit, the angle α of the first dark band being given by the usual formula[19]

$$\sin \alpha = \frac{\lambda}{d} \qquad (3.40)$$

Thus, although before passing the slit the y-component of the momentum of the beam was $p_y = 0$, after diffraction the beam has acquired a y directed momentum which, if we limit ourselves to the main lobe of the diffraction pattern, could be as large as $\pm p \sin \alpha$. Multiplying the two uncertainties we obtain

$$\Delta y \, \Delta p_y = d2p \sin \alpha = 2p\lambda = 2h \qquad (3.41)$$

which is of the right order of magnitude, the exact numerical differences between (3.39) and (3.41) being due to different definitions of measure adopted for Δy and Δp_y in the two cases.

Let us now consider the wave packet (3.19) once again and form a Fourier pair by starting with $\Psi(0, t)$ rather than $\Psi(z, 0)$. We obtain, writing $A(\beta) \, \mathrm{d}\beta = F(\omega) \, \mathrm{d}\omega$,

$$\Psi(0, t) = \Psi(t) = (2\pi)^{-\frac{1}{2}} \int F(\omega) \, \mathrm{e}^{-j\omega t} \, \mathrm{d}\omega \qquad (3.42)$$

$$F(\omega) = (2\pi)^{-\frac{1}{2}} \int \Psi(t) \, \mathrm{e}^{j\omega t} \, \mathrm{d}t \qquad (3.43)$$

A series of transformations similar to those indicated by (3.29)–(3.38) then leads to the following inequality

$$\Delta\omega \, \Delta t \geqslant \tfrac{1}{2} \qquad (3.44)$$

which strongly resembles (3.25), again bearing in mind the somewhat different definitions of $\Delta\omega$ and Δt which have been adopted in the two cases. Multiplying both sides of (3.44) by $\hbar$ we obtain, in view of (3.9),

$$\Delta E \, \Delta t \geqslant \tfrac{1}{2}\hbar \qquad (3.45)$$

which is another well-known expression due to Heisenberg. According to (3.45) there is an upper limit to the accuracy with which we can observe the energy of a particle if the corresponding time of observation is Δt, the minimum value of the product $\Delta E \, \Delta t$ being $\tfrac{1}{2}\hbar$.

Although (3.39) and (3.45) have been derived on the basis of somewhat limited considerations, their validity is quite general and their physical meaning is rather profound. In fact, these inequalities tell us that, however good our means of observation, we can never hope to obtain experimental results for pairs of variables such as position and momentum,

or energy and time, which will jointly give a better accuracy than that
indicated by Heisenberg's uncertainty principle. According to our present
understanding of nature this limitation is quite fundamental and
irrevocable. The reciprocal or complementary nature of such pairs of
variables in any given experiment is often referred to as the *comple-
mentarity principle*.[20]

There is another way of looking at (3.39) and (3.45) which physically
may be even more rewarding. In considering particles of atomic
dimensions, i.e., when the minute value of $h = 6 \cdot 63 \times 10^{-34}$ joule sec (units
of 'action') becomes significant, the mere act of observation affects the
state of the particle in a quantized and unpredictable manner, as was
pointed out in chapter 1, and can no longer be ignored. Thus, if we used,
for example, a beam of light to find the position of a highly polished cube
of steel of reasonable dimensions, we could safely neglect the effect of
light pressure, i.e., of our act of observation. However, if instead of a cube
of steel we have to deal with a single electron, the mere act of shining
even a single quantum of light on it would be sufficient to affect its
position quite appreciably. Thus, if we tried to observe the linear
momentum of the electron to within Δp, we could not simultaneously
determine its position with an accuracy better than Δz given by (3.39).
It is interesting to note that both quantum mechanics and the theory
of relativity are in the nature of fine corrections or generalizations of
classical physics. In both cases we carefully consider the consequences of
a mere act of observation. In the case of quantum mechanics we allow
for the disturbing effect an observation must necessarily have on the
system, the most obvious range of applications covering atomic particles.
In the theory of relativity we specifically allow for the non-infinite
velocity of the light signals which are used for carrying out such observa-
tions, the significant dimensions being astronomic. As a result of these
corrections we are faced in quantum mechanics with the problem of
uncertainty and in relativity with the curious geometrical properties of
space and time.

3.6. The general laws of motion

Let us now consider the quantum mechanical equivalent of Newton's
laws of motion. As far as the First Law is concerned we can usefully
employ the concept of a wave packet of the form (3.19) which is only
valid however when ω and β are independent of z or t, i.e., when the
corresponding particle is free, its potential energy V being either zero or
some other constant. Rewriting (3.19) in the form

$$\Psi(z, t) = (2\pi)^{-\frac{1}{2}} \int (A \, e^{-j\omega t}) \, e^{j\beta z} \, d\beta \qquad (3.19)$$

we obtain for its Fourier transform, by analogy with (3.26) and (3.27),

$$A(\beta)\,e^{-j\omega t} = (2\pi)^{-\frac{1}{2}}\int \Psi(z,\,t)\,e^{-j\beta z}\,dz \qquad (3.46)$$

so that

$$A(\beta) = (2\pi)^{-\frac{1}{2}}\int \Psi(z,\,t)\,e^{j(\omega t - \beta z)}\,dz \qquad (3.46a)$$

We can now show, by substituting (3.46) in (3.19) and making use of the same Fourier pair (3.26), (3.27), that the normalization of Ψ holds for any value of t, provided that (3.18) was satisfied for, say, $t=0$ (see also problem 12). Similarly, although t appears explicitly in (3.46), the functions $A(\beta)$ and A^*A are both independent of time. Thus, from (3.13), the momentum composition of the wave packet associated with a free particle remains unchanged—a statement which seems to provide quite a satisfying quantum mechanical analogue of the constancy of linear momentum of a free particle, which expresses the First Law of motion in classical mechanics. What is the equivalent of the Second Law of motion? We have already tried to derive the corresponding energy relationship (3.11v) on the condition, however, that the energy function V varies with z only slowly and that the mass of the particle m remains constant and independent of either ω or β. We are now going to show that in the case of an arbitrary potential function V, for example that of an electron interacting with the periodically spaced atoms of a crystal lattice, this assumption is no longer valid, so that (3.11v) and, in particular, (3.13), must be amended. In a conservative system the total energy of the particle is given by (3.8v); although the general relationships (3.6), (3.9) and $v=v_g$ are still valid for an arbitrary V, we are no longer permitted to substitute (3.9) in (3.8v) and integrate, as we have done to obtain (3.11v), because the constancy of m is now in question.

Let us consider a model in which the E–β curve is continuous, so that it is possible to define a group velocity v_g which is still identified with the particle velocity v. Substituting (3.9) in (3.6) we obtain

$$v = \frac{d\omega}{d\beta} = \frac{1}{\hbar}\frac{dE}{d\beta} \qquad (3.47)$$

This tells us that, in general, the velocity of a particle is proportional, in a conservative system, to the slope of the total energy function E expressed in terms of β; thus, for a fast moving particle, the total energy of the particle, E, depends quite strongly on the phase constant β of the corresponding Ψ-wave, which appears as a steep portion of the ω–β curve, Fig. 3.1. For a parabolic dispersion curve (3.11v) equation (3.47) still reduces to (3.13).

Let us now differentiate (3.47) with respect to time, in order to obtain a

general expression for the acceleration of a particle subjected to a field of force

$$a = \dot{v} = \frac{1}{\hbar} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\mathrm{d}E}{\mathrm{d}\beta} \right)$$

$$= \frac{1}{\hbar} \dot{\beta} \frac{\mathrm{d}^2 E}{\mathrm{d}\beta^2} \tag{3.48}$$

As usual, the dot is used to indicate a total differential with respect to time. Equation (3.48) shows that, in general, the acceleration of a particle is proportional to the second derivative of the ω–β curve and becomes zero at points of inflexion of that curve. We are now in a position to write a quantum mechanical equivalent of Newton's Law of Force. Writing an expression for the change in the kinetic energy of the particle due to the action of the external force F and substituting from (3.47) we obtain

$$\delta E' = Fv\, \delta t = F \frac{1}{\hbar} \frac{\mathrm{d}E}{\mathrm{d}\beta}\, \delta t \tag{3.49}$$

Since by definition

$$\delta E = \frac{\mathrm{d}E}{\mathrm{d}\beta}\, \delta\beta$$

and the potential energy is independent of β, so that $\delta E = \delta E'$,

$$F\, \delta t = \hbar\, \delta\beta$$

or, in the limit,

$$F = \hbar\dot{\beta} \tag{3.50}$$

Equation (3.50) is the quantum mechanical equivalent of Newton's Second Law of motion. The external force F acts on the particle in such a way that with time it affects the phase constant β of the associated Ψ-wave. The larger the force, the more rapid is the change in the value of β.

If we wish to preserve the formal expression $F = \text{mass} \times \text{acceleration}$ we must introduce the so-called *effective mass* m^*; comparing (3.48) and (3.50) we obtain

$$m^* = \hbar^2 \left/ \frac{\mathrm{d}^2 E}{\mathrm{d}\beta^2} \right. \tag{3.51}$$

The effective mass m^* is a somewhat artificial concept and should be treated with caution. It is associated with a semiclassical type of thinking in which the Ψ-wave is strongly localized to a particle of mass m^*; this mass, however, is not a constant but varies from point to point along the

β-axis depending on the shape of the corresponding E–β curve; by (3.51) it remains constant and equal to m only when the curve is the parabola given by (3.11) or (3.11v). The dependence of the effective mass on the total energy of the particle is such that it can even lead to negative values of m^*. However, in spite of its apparent weaknesses, this concept has proved to be invaluable in the discussion of electrical conduction in solids.

For the motion of a particle in three dimensions we obtain, using identical reasoning, the following expressions which are physically equivalent to (3.47)–(3.51): velocity

$$\mathbf{v} = \text{grad}_k\, \omega = \frac{1}{\hbar}\, \text{grad}_k\, E \tag{3.47}$$

acceleration

$$\mathbf{a} = \dot{\mathbf{v}} = \frac{1}{\hbar}\frac{d}{dt}\,(\text{grad}_k\, E)$$

$$= \frac{1}{\hbar}\,\dot{\mathbf{k}}\,\text{grad}_k\, \text{grad}_k\, E \tag{3.48}$$

force equation

$$\mathbf{F} = \hbar\dot{\mathbf{k}} \tag{3.50}$$

effective mass

$$m^* = \hbar^2 \{\text{grad}_k\, \text{grad}_k\, E\}^{-1} \tag{3.51}$$

The total energy of the particle $E = E(\mathbf{k})$ is now a function of three independent variables, k_x, k_y, k_z, the components of the propagation vector of the relevant Ψ-wave. The double gradient operator $\text{grad}_k\, \text{grad}_k\, E$ is then a second order tensor which, depending on the properties of the system, may possess various degrees of symmetry. The effective mass is then expressed in terms of the corresponding reciprocal tensor.

3.7. Observables and operators

One can introduce the concepts of operators and observables in a number of different ways, one of the most general, not to say beautiful, being that due to Dirac.[21] However, in the context of this book, it seems best to introduce them as one more consequence of the wave-mechanical representation of quantum mechanics.

We have already stated that, following Born,[14] the only physical significance which can be attached to a Ψ-wave relates the square of its amplitude, $\Psi^*\Psi$, to the probability density function describing the position in space of the corresponding particle. Furthermore, it was pointed out in section 3.3, that in general one can only estimate the

probability of occurrence of different possible results of a single experiment and never its exact value. Thus, knowing $\Psi^*\Psi$, we can calculate various moments of the corresponding distribution, as indicated in appendix 3, the most interesting of them, in this case, being the first moment, or the mean position of the particle

$$\langle z \rangle = \int \Psi^* z \Psi \, dz \qquad (3.52)$$

or, in three dimensions,

$$\langle \mathbf{r} \rangle = \int \Psi^* \mathbf{r} \Psi \, d\mathbf{r} \qquad \mathbf{(3.52)}$$

Thus, in physical terms, if we performed a large number of identical experiments with identical particles or systems, the object of each experiment being the measurement of position of the particle, we would discover that the probability of occurrence of each result would be given by the function $\Psi^*\Psi$ and the mean position of the particle by (3.52) or (**3.52**). The quantities defined in a manner similar to (3.52) or (**3.52**) are called *observables* since only *their* values can be safely predicted as the outcome of a large number of identical experiments. The observables, being related to physical measurements, cannot be complex quantities but must be real. The quantity z or $\mathbf{r}$ in the above equations is called an *operator* since it 'operates' on the function Ψ which follows it, changing it from Ψ to $z\Psi$ or $\mathbf{r}\Psi$. Although in this context the definition of an operator may seem somewhat trivial, we shall shortly see that in quantum mechanics operators often contain differentiation, so that, for example, $x(\partial/\partial x)$ operating on Ψ may give quite a different result from $(\partial/\partial x)x$ operating on the same function Ψ. Then the operators acquire very interesting properties which are discussed in this section.

Let us repeat here that, although the reader may be familiar with the concepts of probability and probability density function, he may tend to regard them as a measure of his ignorance of the microscopic structure of the system. By that one usually means that there is no natural limit to the amount of detail which one could learn, at least in principle, provided one chose to do so. In quantum mechanics, the situation is quite different, and equations of the type (3.52) in fact provide an inherent limitation on the amount of detail one can obtain about the system. Some like to refer to them as the only 'windows' through which one can observe the microscopic world of quantum mechanics.

We have already pointed out in discussing (3.28) that A^*A is a probability density function of the phase constant β, the mean value of the linear momentum of the free particle being given, from (3.13), by

$$\langle p \rangle = \hbar \langle \beta \rangle = \hbar \int A^*(\beta) \beta A(\beta) \, d\beta \qquad (3.53)$$

or, in three dimensions, following our convention on β and **k** explained on p. 21

$$\langle \mathbf{p} \rangle = \hbar \langle \mathbf{k} \rangle = \hbar \int A^*(\mathbf{k}) \mathbf{k} A(\mathbf{k}) \, d\mathbf{k} \tag{3.53}$$

However, most calculations in quantum mechanics are carried out in terms of Schrödinger's equation and the corresponding Ψ functions. In order to avoid solving another differential equation for $A(\beta)$, we invariably choose to express (3.53) in terms of $\Psi^*\Psi$ rather than A^*A. Fortunately, there is a general theorem concerning Fourier pairs,[18] an example of which was quoted as (3.37) and used in the derivation of the Schwarz inequality (3.38). Substituting for A^* in (3.53) from (3.52) we obtain

$$\langle p \rangle = \hbar \int \left\{ (2\pi)^{-\frac{1}{2}} \int \Psi^* \, e^{-j(\omega t - \beta z)} \, dz \right\} \beta A \, d\beta$$

$$= \hbar \int \Psi^* \left\{ (2\pi)^{-\frac{1}{2}} \int A\beta \, e^{-j(\omega t - \beta z)} \, d\beta \right\} dz$$

$$= \frac{\hbar}{j} \int \Psi^* \frac{\partial \Psi}{\partial z} \, dz$$

$$= \int \Psi^* \hat{p} \Psi \, dz \tag{3.54}$$

where

$$\hat{p} = \frac{\hbar}{j} \frac{\partial}{\partial z} \tag{3.55}$$

is a new operator, the corresponding symbol being marked with an accent. Thus, if we wish to use the Ψ representation, as we invariably do in practice, for calculating the mean value of the linear momentum of a particle, we must use the operator $\hat{p}$ in place of p.

Carrying out similar calculations for the three-dimensional case we obtain from (**3.19**) and a suitable equivalent of (3.46a)

$$\hat{p}_x = \frac{\hbar}{j} \frac{\partial}{\partial x}, \quad \hat{p}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

$$\hat{p}_y = \frac{\hbar}{j} \frac{\partial}{\partial y}, \quad \hat{p}_y^2 = -\hbar^2 \frac{\partial^2}{\partial y^2}$$

$$\hat{p}_z = \frac{\hbar}{j} \frac{\partial}{\partial z}, \quad \hat{p}_z^2 = -\hbar^2 \frac{\partial^2}{\partial z^2}$$

or, using vector notation

$$\hat{\mathbf{p}} = \frac{\hbar}{j} \nabla, \quad \hat{\mathbf{p}}^2 = -\hbar^2 \nabla^2 \tag{3.55}$$

Similarly, using the accent notation, we find from (3.52) that

$$\hat{z} = z \tag{3.56}$$

$$\hat{V}(z, t) = V(z, t) \tag{3.57}$$

or, in three dimensions,

$$\hat{\mathbf{r}} = \mathbf{r} \tag{3.56}$$

$$\hat{V}(\mathbf{r}, t) = V(\mathbf{r}, t) \tag{3.57}$$

the potential energy V being a function of (z, t) or $(\mathbf{r}, t)$ only.

Finally, let us derive an expression for the operator which would enable us to calculate the mean energy of a particle in terms of its wave function Ψ. Taking the probability density function A^*A, since $\omega = E/\hbar$ is a function of β, and bearing in mind (3.19) and (3.46a), we obtain

$$
\begin{aligned}
\langle E \rangle = \hbar \langle \omega \rangle &= \hbar \int A^*(\beta) \omega A(\beta) \, d\beta \\
&= \hbar \int \left\{ (2\pi)^{-\frac{1}{2}} \int \Psi^* \, e^{-j(\omega t - \beta z)} \, dz \right\} \omega A \, d\beta \\
&= \hbar \int \Psi^* \left\{ (2\pi)^{-\frac{1}{2}} \int A\omega \, e^{-j(\omega t - \beta z)} \, d\beta \right\} dz \\
&= j\hbar \int \Psi^* \frac{\partial \Psi}{\partial t} \, dz \\
&= \int \Psi^* \hat{E} \Psi \, dz \tag{3.58}
\end{aligned}
$$

so that the energy operator is

$$\hat{E} = j\hbar \frac{\partial}{\partial t} \tag{3.59}*$$

In classical mechanics, it is often useful to introduce the concept of the *Hamiltonian*,[22] which, in the case of a single particle subjected to a field of force defined by the function $V(z, t)$ is simply given by

$$H = \frac{p^2}{2m} + V(z, t) \tag{3.60}$$

For conservative systems, i.e., when V is a function of position only, the Hamiltonian is equal to the total energy of the system, $H = E$, and (3.60)

* Some authors do not recognize this as a genuine operator, since, in classical mechanics, t is not a dynamical variable in the same sense as z or p are, the latter representing the inherent properties of a particle.

reduces to (3.8v). Let us define the Hamiltonian operator by adding accents over all terms in (3.60). Then, substituting from (3.55), (3.56), and (3.59) we obtain

$$\hat{H}\Psi = \hat{E}\Psi = \frac{\hat{p}^2}{2m}\Psi + \hat{V}\Psi$$

$$j\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial z^2} + V\Psi \tag{3.60a}$$

which is, of course, the Schrödinger equation (3.22). Since, as we have already pointed out, this equation is found to be valid in general, i.e., when V is a function of $\mathbf{r}$ and t, as well as for the special case of a free particle used in the above derivations, we can extend the definition of the $\hat{p}$ operator to cover the general case, and also introduce the Hamiltonian operator defined by

$$\hat{H} = j\hbar\frac{\partial}{\partial t} \tag{3.61}$$

There is one important consequence of the algebraic form of the operators containing the differential sign, which limits the type of function admissible as a physically meaningful solution of the Schrödinger wave equation. We already know from the normalization requirement (**3.19**) that the solutions Ψ must all vanish at $\pm\infty$. We now find that Ψ, $\nabla\Psi$ must be single valued to provide an unambiguous physical meaning for $\Psi^*\Psi$, $\mathbf{p}$ and continuous, to avoid infinite values of $\mathbf{p}$. For the same reason (3.61) imposes similar conditions on Ψ and $\partial\Psi/\partial t$ as functions of time. These restrictions, however, are not very severe and lead to solutions in terms of functions which are generally called 'well behaved'.

So far we have been able to discuss quantum mechanics in terms of familiar algebraic concepts, but at this stage we should broaden our outlook somewhat and consider some of the more general properties of operators and observables. We have just seen that operators can be functions not only of the independent variables z or $\mathbf{r}$ but also of the derivatives $\partial/\partial z$ and $\partial/\partial t$, as, for example, in the case of (3.55) and (3.61). Let us now consider an operator of the form $\hat{O} = (\partial/\partial z)z$; then, for any function $S(z)$,[23]

$$\hat{O}S(z) \equiv \frac{\partial}{\partial z}\left[zS(z)\right]$$

$$= S(z) + z\frac{\partial S(z)}{\partial z} \tag{3.62}$$

Since (3.62) is valid for any $S(z)$, we could write it in a more symbolic way as an *operator equation*

$$\hat{O} \equiv \frac{\partial}{\partial z}z = 1 + z\frac{\partial}{\partial z} \tag{3.62a}$$

Clearly, the two sides of (3.62) or (3.62a) have different algebraic forms, unless $S(z)$ is carefully chosen. In general, to each operator $\hat{O}$ belongs a set of numbers O_n, called the *eigenvalues* and a set of functions $S_n(z)$, called the *eigenfunctions*, such that

$$\hat{O}S_n = O_nS_n \qquad (3.63)$$

the equation being called the *eigenvalue equation* of the operator $\hat{O}$. Thus, among all the arbitrary functions $S(z)$ the eigenfunctions of the operator are defined by the property that they remain unaltered by the operation, apart from being multiplied by a constant, called the eigenvalue. In the case of (3.62) the eigenfunctions are given by solutions of the differential equation

$$S_n(z) + z\,\frac{\partial S_n(z)}{\partial z} = O_nS_n(z) \qquad (3.63a)$$

i.e., by

$$S_n(z) = z^{O_n - 1} \qquad (3.64)$$

the actual eigenvalues O_n being determined by the boundary conditions.

Let us now limit ourselves to the so-called linear operators, which have the following properties[24]:

(1) $\hat{O}$ operating on any wave function Ψ_1 yields another wave function Ψ_2, i.e., $\hat{O}\Psi_1 = \Psi_2$, where, in general, $\Psi_1 \neq \Psi_2$.
(2) $\hat{O}(\Psi_1 + \Psi_2) = \hat{O}\Psi_1 + \hat{O}\Psi_2$.
(3) $c\hat{O}\Psi_1 = \hat{O}(c\Psi_1)$, where c is a constant.

The first condition now ensures that we can put the wave functions Ψ_n in place of S_n in (3.63) so that now

$$\hat{O}\Psi_n = O_n\Psi_n \qquad (3.65)$$

Possibly the best known example of such an eigenvalue equation is provided by the Hamiltonian operator (3.61), namely,

$$j\hbar\,\frac{\partial \Psi_n}{\partial t} \equiv \hat{H}\Psi_n = E_n\Psi_n \qquad (3.65a)$$

In this case, using the accepted notation, the energy values E_n are the eigenvalues of the operator $\hat{H}$.

It is usual now to assume[25,26] that to any dynamical variable corresponds a linear operator $\hat{O}$, that the only possible result of a single observation of this variable is one of the corresponding eigenvalues O_n and that the average value of a large number of similar observations carried out on identical systems, all in an arbitrary state defined by a wave function Ψ, is given by

$$\langle O \rangle = \int \Psi^*\hat{O}\Psi\,d\mathbf{r} \qquad (3.66)$$

which is a general form of (3.52), (3.54), or (3.58). If the observations represented by the operator $\hat{O}$ are performed on identical systems, all in an eigenstate Ψ_n, then, in view of (3.65), equation (3.66) reduces to

$$\langle O \rangle = \int \Psi_n^* \hat{O} \Psi_n \, d\mathbf{r}$$

$$= \int \Psi_n^* O_n \Psi_n \, d\mathbf{r}$$

$$= O_n \int \Psi_n^* \Psi_n \, d\mathbf{r}$$

$$= O_n \tag{3.66a}$$

in view of the normalization conditions (3.18). In this special case the observable is equal to the eigenvalue O_n corresponding to the eigenstate n defined by the wave (eigen) function Ψ_n. Furthermore, since for any value of an integer k, we also have

$$\langle O^k \rangle = \int \Psi_n^* \hat{O}^k \Psi_n \, d\mathbf{r}$$

$$= \int \Psi_n^* O_n^k \Psi_n \, d\mathbf{r}$$

$$= O_n^k \int \Psi_n^* \Psi_n \, d\mathbf{r}$$

$$= O_n^k \tag{3.66b}$$

the variance (see appendix 3) $\sigma^2 = \langle O^2 \rangle - \langle O \rangle^2$ and all the higher differences $\langle O^k \rangle - \langle O \rangle^k$ are now equal to zero. Hence the associated probability density function describing the probability (or frequency) of occurrence of different values of the variable O now degenerates into an infinitely narrow pulse (a Dirac delta function) situated at the point $O = O_n$, the function being zero everywhere else.[27] In general, the mere fact of measurement in quantum mechanics forces the system under observation into one of its eigenstates which is appropriate to the variable being measured. If the system already is in the appropriate eigenstate, then the value of the corresponding variable must be one of the eigenvalues O_n and the result of a subsequent measurement of this variable can only give this value, even though the physical conditions for such a measurement may be somewhat unrealistic (e.g., for a system in an energy eigenstate, say, E_n, $\Delta t \rightarrow \infty$ when $\sigma_E = \Delta E = 0$ from (3.45)). In general the probability of occurrence of an eigenvalue O_n is given by the appropriate probability distribution or probability density function, depending on whether the distribution is discrete or continuous, the latter point

depending on the physical properties of the system expressed in the form of the boundary conditions which have to be satisfied by the appropriate eigenvalue equation.

Finally, let us consider one more consequence of the requirement that the observables must be real, i.e., that $\langle O \rangle = \langle O \rangle^*$. From this and (3.66) we find that the only operators which are acceptable in quantum mechanics must satisfy the following condition

$$\int \Psi^* \hat{O} \Psi \, d\mathbf{r} = \int \Psi \hat{O}^* \Psi^* \, d\mathbf{r} = \int \Psi (\hat{O}\Psi)^* \, d\mathbf{r} \qquad (3.67)$$

Such operators are called Hermitian, although it has been suggested that a more descriptive name for them might have been 'real operators'.[28]

3.8. Commutators

We have already pointed out in chapter 1 that an experiment or observation in quantum mechanics must cause a change, however small, in the system under observation. Thus, if we wish to perform two observations in succession, the order in which they follow one another may well cause a difference to the final outcome of the experiment. In the previous section we have already agreed that all physically meaningful observations can be represented by linear operators, there being one operator to each observable property of the system. It would thus follow that, in general, for two linear operators $\hat{A}$ and $\hat{B}$ we will have $\hat{A}\hat{B} \neq \hat{B}\hat{A}$.

The most common arrangement of linear operators in quantum mechanics is the so-called *commutator* of $\hat{A}$ and $\hat{B}$, defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \qquad (3.68)$$

It may be added that commutators are the quantum mechanical equivalents of Poisson brackets, as is explained more fully in appendix 2. Since, as we have seen, the operators $\hat{A}$ and $\hat{B}$ may specify differentiation, it is fairly obvious that (3.68) may well be different from zero (see, for example, problem 18), in accordance with the physical requirements. In short, in the case of the linear operators of quantum mechanics the usual commutative law of algebra may not apply, a situation which is somewhat similar to that encountered in the algebra of matrices. As we shall see later (section 7.5) this similarity between the behaviour of matrices and operators has a much deeper significance in quantum mechanics.

One of the most important examples of a commutator in quantum mechanics is that provided by the operators $\hat{\mathbf{q}} = (q_i, q_j, q_k)$ and $\hat{\mathbf{p}} = (p_i, p_j, p_k)$ representing the usual position $\mathbf{q}$ and momentum $\mathbf{p}$ 'canonically conjugate coordinates' of classical mechanics.[29] (For cartesian coordinates $\mathbf{q} = \mathbf{r}$ and $\mathbf{p} = m\mathbf{v}$; for cylindrical coordinates $\mathbf{q} = (r, \theta, z)$ and $\mathbf{p} = (m\dot{r}, mr^2\dot{\theta}, m\dot{z})$ and so on.) From the definition of a commutator (3.68) and from (3.55)

and (3.56) we now obtain

$$[\hat{q}_i, \hat{p}_j]\Psi(\mathbf{q}) = (\hat{q}_i\hat{p}_j - \hat{p}_j\hat{q}_i)\Psi(\mathbf{q})$$

$$= \frac{\hbar}{j}q_i\frac{\partial}{\partial q_j}\Psi(\mathbf{q}) - \frac{\hbar}{j}\frac{\partial}{\partial q_j}q_i\Psi(\mathbf{q})$$

$$= j\hbar\Psi(\mathbf{q})\frac{\partial}{\partial q_j}q_i$$

or, symbolically,

$$[\hat{q}_i, \hat{p}_j] = j\hbar \quad \text{if} \quad i = j$$

$$= 0 \quad \text{if} \quad i \neq j \tag{3.69}$$

Similarly, putting $\hat{q}$ for $\hat{p}$ in (3.69), or vice versa, we obtain two more important relations

$$[\hat{q}_i, \hat{q}_j] = 0 \tag{3.70}$$

$$[\hat{p}_i, \hat{p}_j] = 0 \tag{3.71}$$

Equation (3.69) together with other similar expressions clearly show that the conjugate pairs of variables, such as x and p_x, or y and p_y, do not commute, i.e., the commutator of the corresponding operators is different from zero. This is closely related to the fact that in quantum mechanics there is a fundamental limit to the accuracy with which such conjugate variables can be simultaneously observed or measured, as is indicated by the uncertainty relationships (3.39) and (3.45).[30] The commutators logically describe the consequences of the uncertainty principle when applied not to simultaneous but to successive measurements of conjugate variables.

Equation (3.69) provides us with an excellent opportunity to obtain some measure of the uncertainties involved in quantum mechanics. Since $\hbar = 1.05 \times 10^{-34}$ joule sec the difference between $p_i q_j$ and $q_j p_i$ can only be significant when they are both of this order of magnitude, i.e., when the position and momentum of a particle are measured on the atomic scale, the mass of an electron being, for example, equal to 9.11×10^{-31} kg. In the case of even the lightest dust particles, their momentum alone is invariably numerically larger than $\hbar$ by many orders of magnitude, so that the right-hand side of (3.69) would be indistinguishable from zero for all practical purposes. Thus in trying to measure the position and momentum of such a relatively large particle we do not have to worry about the basic limitation on accuracy introduced by the very act of measurement, as we have to in the case of atomic particles. As we have already pointed out earlier, this tendency for the laws of quantum mechanics to approach asymptotically those of classical mechanics is often referred to as the correspondence principle.

Finally, let us consider the experimental equivalent of (3.69) which would be the successive observation of the position and momentum of a particle. If the particle is stationary and we observe its position first and its linear momentum afterwards, as is indicated by the first term of the commutator (3.69), then, due to the disturbance of the position of the particle caused by interaction with a photon of light necessary for the mere act of observation, the particle will have acquired some linear momentum, even if it was originally stationary. On the other hand, if we measured its momentum first and the position afterwards, as indicated by the second term in the commutator (3.69), the corresponding value of the linear momentum would be approximately zero, irrespective of the subsequent position of the particle. Since the outcome of the combined experiment would be different in the two cases, the corresponding commutator (3.69), which is a mathematical symbol of the underlying physical reality, is different from zero.

Let us now consider the following problem. In general, the mean value of a linear operator, the observable $\langle O \rangle$, is a function of time. Differentiating (3.66) partially with respect to t we obtain

$$\frac{\partial}{\partial t} \langle O \rangle = \int \left(\frac{\partial \Psi^*}{\partial t} \hat{O} \Psi + \Psi^* \frac{\partial \hat{O}}{\partial t} \Psi + \Psi^* \hat{O} \frac{\partial \Psi}{\partial t} \right) d\mathbf{r} \qquad (3.72)$$

Substituting from (3.61) and its complex conjugate we obtain, bearing in mind the definition of $\langle O \rangle$,

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{j}{\hbar} \int (\hat{H} \Psi^* . \hat{O} \Psi - \Psi^* \hat{O} \hat{H} \Psi) \, d\mathbf{r} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle \qquad (3.73)$$

the dot indicating ordinary multiplication for clarity. But, according to Green's theorem, if two functions u and v approach zero at infinity rapidly enough[31]

$$\int u \nabla^2 v \, d\mathbf{r} = \int v \nabla^2 u \, d\mathbf{r} \qquad (3.74)$$

Making use of (3.74) and of the three-dimensional equivalent of (3.60a) we obtain

$$\int \hat{H} \Psi^* . \hat{O} \Psi \, d\mathbf{r} = -\frac{\hbar^2}{2m} \int \hat{O} \Psi . \nabla^2 \Psi^* \, d\mathbf{r} + \int V \Psi^* . \hat{O} \Psi \, d\mathbf{r}$$

$$= -\frac{\hbar^2}{2m} \int \Psi^* \nabla^2 \hat{O} \Psi \, d\mathbf{r} + \int \Psi^* V . \hat{O} \Psi \, d\mathbf{r}$$

$$= \int \Psi^* \hat{H} \hat{O} \Psi \, d\mathbf{r}$$

Substituting this in (3.73) we finally obtain, changing $\partial/\partial t$ to d/dt, since $\langle O \rangle$ is a function of time only,

$$
\begin{aligned}
\frac{d}{dt} \langle O \rangle &= \frac{j}{\hbar} \int \Psi^*(\hat{H}\hat{O} - \hat{O}\hat{H})\Psi \, d\mathbf{r} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle \\
&= \frac{j}{\hbar} \langle (\hat{H}\hat{O} - \hat{O}\hat{H}) \rangle + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle \\
&= \left\langle \frac{j}{\hbar} [\hat{H}, \hat{O}] + \frac{\partial \hat{O}}{\partial t} \right\rangle
\end{aligned}
\tag{3.75}
$$

Equation (3.75) is very useful and quite general. It can be applied straight away to prove the persistence of normalization and the conservation of energy. If we put $\hat{O} = 1$ in (3.75) we obtain, since now $[\hat{H}, \hat{O}] = 0$ and $\partial \hat{O}/\partial t = 0$,

$$
\frac{d}{dt} \langle O \rangle = \frac{d}{dt} \int \Psi^*\Psi \, d\mathbf{r} = 0
\tag{3.76}
$$

We have already shown before using the Fourier pairs (3.19) and (3.27) that (3.76) is true for a free particle, but the present method is much more general. Similarly, if we put $\hat{O} = \hat{H}$ in (3.75) we obtain since again $[\hat{H}, \hat{H}] = 0$ and $\partial \hat{H}/\partial t = 0$,

$$
\frac{d}{dt} \langle O \rangle = \frac{d}{dt} \langle H \rangle = 0
\tag{3.77}
$$

provided that the Hamiltonian operator $\hat{H}$ does not depend on time explicitly. We have already used this theorem in deriving (3.60a) by putting the Hamiltonian $H = E$, where E is the total energy of the system.

Similarly, putting $\hat{O} = \hat{x}$ in (3.75) we obtain

$$
\begin{aligned}
[\hat{H}, \hat{x}] &= \left[\left\{ \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \hat{V} \right\}, \hat{x} \right] \\
&= \left[\frac{1}{2m} \hat{p}_x^2, \hat{x} \right] \\
&= \frac{1}{2m} (\hat{p}_x[\hat{p}_x, \hat{x}] + [\hat{p}_x, \hat{x}]\hat{p}_x) \\
&= \frac{1}{m} \frac{\hbar}{j} \hat{p}_x
\end{aligned}
\tag{3.78}
$$

where we have used (3.69)–(3.71) and the identity

$$
[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}
$$

(See also problem 19.) Thus, from (3.75) we can now write

$$m \frac{d}{dt} \langle x \rangle = \langle p_x \rangle \qquad (3.79)$$

similar expressions being valid for the remaining two components of position and momentum, so that in vector notation

$$m \frac{d}{dt} \langle \mathbf{r} \rangle = \langle \mathbf{p} \rangle \qquad (3.79)$$

This expression, which resembles the definition of linear momentum in classical mechanics, again shows that in quantum mechanics we can only draw predictable conclusions concerning averages or expectation values based on a large number of identical experiments, and not, in general, on a single experiment.

Also putting $\hat{O} = \hat{p}_x$ in (3.75) we obtain

$$[\hat{H}, \hat{p}_x] = \left[\left\{ \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \hat{V} \right\}, \hat{p}_x \right]$$

$$= [\hat{V}, \hat{p}_x]$$

$$= -\frac{\hbar}{j} \frac{\partial V}{\partial x} \qquad (3.80)$$

so that from (3.75) we now obtain for a time-independent V

$$\frac{d}{dt} \langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \qquad (3.81)$$

or, in vector notation, bearing in mind that the same reasoning applies to the remaining two components of the linear momentum vector,

$$\frac{d}{dt} \langle \mathbf{p} \rangle = -\langle \nabla V \rangle \qquad (3.81)$$

This is the exact quantum-mechanical equivalent of Newton's Second Law of motion, except that now again it refers to the average obtained for a large number of identical experiments, and not to a single experiment. Both (3.79) and (3.81) are often referred to as *Ehrenfest's Theorem*. It should be noted here that as long as (3.13) holds, i.e., as long as there are no violent changes in V, (3.81) goes over into (3.50) which was derived in section 3.6 using an entirely different mode of reasoning.

Finally, let us consider an operator defined by

$$\frac{d\langle O \rangle}{dt} = \int \Psi^* \frac{d\hat{O}}{dt} \Psi \, d\mathbf{r}$$

Substituting this in (3.75) we find, since the new expression must be valid for all wave functions Ψ,

$$\frac{d\hat{O}}{dt} = \frac{j}{\hbar}(\hat{H}\hat{O}-\hat{O}\hat{H})+\frac{\partial\hat{O}}{\partial t} \tag{3.82}$$

Equation (3.82) clearly shows that if an operator is a constant of motion, $d\hat{O}/dt=0$, it must commute with $\hat{H}$. Also, comparing (3.75) and (3.82) we find that Ehrenfest's Theorem (3.79), (3.81) can be written symbolically by substituting corresponding operators in place of the expectation values of the variables. Furthermore, putting $\hat{O}=\hat{q}_i$ or $\hat{O}=\hat{p}_i$ in (3.82), where $\hat{q}_i$ and $\hat{p}_i$ are respectively the canonically conjugate position and momentum operators, we obtain the important quantum mechanical equivalents of Hamilton's equations (A2.4) in appendix 2:

$$\frac{d\hat{q}_i}{dt} = \frac{j}{\hbar}(\hat{H}\hat{q}_i-\hat{q}_i\hat{H}) \tag{3.83a}$$

$$\frac{d\hat{p}_i}{dt} = \frac{j}{\hbar}(\hat{H}\hat{p}_i-\hat{p}_i\hat{H}) \tag{3.83b}$$

Comparing the two expressions for the Hamilton equations we find that the Poisson brackets of classical mechanics go over into $-(j/\hbar)$ multiplied by the corresponding commutators of quantum mechanics. The general validity of this theoretical deduction has been repeatedly confirmed by experimental results.

Problems

1. Show by differentiating partially with respect to z and t that (3.2) is the general solution of (3.1).

2. Differentiate (3.19) partially with respect to z and t and show that it satisfies a wave equation of the type (3.1). Why is this equation not acceptable in place of Schrödinger's equation?

3. Carrying out the substitutions indicated by (3.20)–(3.22) derive (3.23) from the complex conjugate of (3.19).

4. Show, by writing $\Psi=a+jb$ or $\Psi^*=a-jb$, that (3.22) and (3.23) each gives rise to the same pair of partial differential equations. Why is this so?

5. Derive (3.22) and (3.23) from (3.19) and its complex conjugate.

6. Show that for a wave train of amplitude A, frequency v_0 and duration from $-\frac{1}{2}\Delta t$ to $+\frac{1}{2}\Delta t$ the frequency spectrum function is given by $F(v)=[A\,\Delta t\,\sin\frac{1}{2}(\omega_0-\omega)\,\Delta t]/\frac{1}{2}(\omega_0-\omega)\,\Delta t$. Taking the main lobe of the distribution as Δv show that $\Delta t\,\Delta v=2$. Why does this differ from (3.25)?

7. Discuss the properties of a probability density function $f(x)$. What is its physical significance? Why does it always have to be real, positive, and less than one?

8. A function related to $f(x)$ and called the distribution function is usually defined as

$$F(x) = \int_0^x f(x)\,dx$$

What is the physical meaning of $F(x)$?

9. What is meant by the mean or expectation value $\langle x \rangle$ calculated with respect to a probability density function $f(x)$? (The reader may use here the definition of probability as a limit of the 'frequency of occurrence'.) What is meant by $\langle x^2 \rangle$?

10. Discuss the difference between ordinary and central moments of a distribution. What is meant by the standard deviation σ, where $\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$?

11. Show that the substitutions (3.31), (3.32) transform (3.29), (3.30) into (3.33), (3.34). Does this affect the generality of (3.39)?

12. Is it possible to obtain (3.45) directly from (3.39) or (**3.39**) without using the Fourier pair (3.42), (3.43)? What are the objections against adopting such a procedure?

13. Prove with the help of (3.19), (3.26), (3.27), and (3.46a) that, in general,

$$\int \Psi^*(z, t)\Psi(z, t)\,dz = 1$$

provided it is satisfied for say $t=0$. Prove a similar theorem for $\Psi(\mathbf{r}, t)$.

14. Show that, in general, for a Fourier pair

$$\psi(t) = (2\pi)^{-\frac{1}{2}} \int \phi(\omega)\,e^{j\omega t}\,d\omega, \quad \phi(\omega) = (2\pi)^{-\frac{1}{2}} \int \psi(t)\,e^{-j\omega t}\,dt$$

we have

$$\int \phi^* \omega^n \phi\,d\omega = (-j)^n \int \psi^* \frac{d^n}{dt^n} \psi\,dt$$

$$\int \psi^* t^n \psi\,dt = j^n \int \phi^* \frac{d^n}{d\omega^n} \phi\,d\omega$$

provided

$$\int \psi^* \psi\,dt = \int \phi^* \phi\,d\omega$$

15. Show, using (**3.19**) and a three-dimensional equivalent of (3.46a) that (**3.55**) are the correct expressions for the operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{p}}^2$.

16. Show, integrating (3.51) twice with respect to β, that if $m^* = m$, the ω–β curve must be a parabola. (Neglect the relativity correction!)

17. Write out in full the operators defined by (3.47) and (3.48). What does it mean that m^* is a tensor? How literally can we take the physical meaning of 'mass' in these circumstances? Can we represent $E = E(\mathbf{k})$ graphically? If not, why not? Could we find some other model for the function?

18. Calculate with the help of an arbitrary function $f(x)$ the commutator $[\hat{A}, \hat{B}]$ for $\hat{A} = x$ and $\hat{B} = \partial/\partial x$.

19. Using an arbitrary function $f(x, y)$ show by analogy that, in general,

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$$
$$[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$$
$$[a, \hat{A}] = 0$$
$$[a\hat{A}, \hat{B}] = a[\hat{A}, \hat{B}]$$
$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$$

where a is a constant, $\hat{A} = x$, $\hat{B} = \partial/\partial x$, and $\hat{C} = \partial/\partial y$.

20. Show that (A2.2) and (A2.4) in appendix 2 are in fact equivalent.

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4. The Stationary State

In the previous chapter we noted the close analogy between the wave concepts of quantum mechanics and the corresponding ideas in electromagnetic theory. This purely mathematical similarity will now help us in the discussion and understanding of the quantum-mechanical concept of a stationary state. As suitable examples we will consider the cases of a bound particle in various potential wells: rectangular, parabolic (harmonic oscillator), and hyperbolic (hydrogen atom), and a free particle encountering a rectangular potential barrier. The concept of angular momentum is also discussed in the last section.

4.1. A resonant cavity

In the electromagnetic theory of resonant cavities it is usual to begin with the wave equation for the **E** and **H** components of the electromagnetic field, **E** and **H** respectively representing the electric and magnetic field vectors. Usually it is sufficient to solve the wave equation for a single component of **E** or **H**, and to obtain the remaining components of the field from the solution. This procedure is made possible by the close relationship between different components of the electromagnetic field embodied in Maxwell's equations. Therefore, in practice, the problem is often reduced to that of solving a single scalar wave equation, but for two different sets of boundary conditions each satisfied by a suitable component of **E** or **H**. If we use F to represent either of the two components, the following wave equation has to be solved in general.

$$\nabla^2 F - \frac{1}{c^2}\frac{\partial^2 F}{\partial t^2} = 0 \tag{4.1}$$

In view of the well known properties of the Fourier series, let us assume that all quantities vary with time as $\exp(-j\omega t)$; (4.1) then reduces to

$$\nabla^2 f + k^2 f = 0 \tag{4.2}$$

where

$$k^2 = \left(\frac{\omega}{c}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2 \tag{4.3}$$

is the square of the phase constant **k** and f is the amplitude of F.

Consider a resonant cavity which is in the form of a rectangular metal

box with one corner at the origin and with edges along the x-, y-, and z-axes, as shown in Fig. 4.1. If the edges are of lengths a_x, a_y, and a_z respectively, then, in the case of the electric field component, the following boundary conditions must be satisfied:

$$f = 0 \quad \text{at} \quad x = 0, \quad x = a_x$$
$$y = 0, \quad y = a_y$$
$$z = 0, \quad z = a_z \qquad (4.4)$$

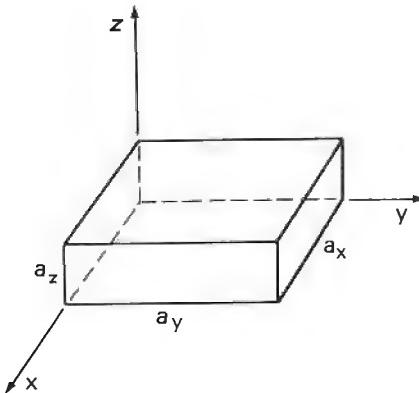Assume that f can be expressed as a product of three functions,

$$f = X(x)Y(y)Z(z) \qquad (4.5)$$

Fig. 4.1. A resonant cavity in the form of a hollow rectangular box.

The partial differential equation (4.2) then reduces to a set of three ordinary differential equations

$$\frac{X''}{X} + k_x^2 = 0$$

$$\frac{Y''}{Y} + k_y^2 = 0 \qquad (4.6)$$

$$\frac{Z''}{Z} + k_z^2 = 0$$

where the double primes signify a second derivative with respect to the argument and

$$k_x^2 + k_y^2 + k_z^2 = k^2 \qquad (4.7)$$

Equations (4.6) can be solved quite easily giving, in general,

$$X = A_x \cos k_x x + B_x \sin k_x x$$
$$Y = A_y \cos k_y y + B_y \sin k_y y \qquad (4.8)$$
$$Z = A_z \cos k_z z + B_z \sin k_z z$$

Substituting the boundary conditions (4.4) we obtain from (4.5) and (4.8)

$$f = B_x B_y B_z \sin \frac{l\pi}{a_x} x \sin \frac{m\pi}{a_y} y \sin \frac{n\pi}{a_z} z \qquad (4.9)$$

which is a solution of (4.2) and represents a standing wave inside the metal box. Here l, m, n are integers, since from (4.4) the walls must coincide with the nodes of the standing wave and, by definition, we can only accommodate an integral number of half-wavelengths between any two nodes.

The electric field inside the cavity is now given by the real or imaginary part of $F = f \exp(-j\omega t)$, the frequency of oscillations from (4.3) and (4.7) being equal to

$$\omega^2 = c^2 k^2 = c^2 \left\{ \left(\frac{l\pi}{a_x} \right)^2 + \left(\frac{m\pi}{a_y} \right)^2 + \left(\frac{n\pi}{a_z} \right)^2 \right\} \qquad (4.10)$$

Since l, m, n are integers the solutions of (4.2) only exist for certain specific values of the parameter $\omega = 2\pi\nu$. These values of ν are called the resonant frequencies of the cavity and, mathematically speaking, are the eigenvalues of (4.2). Thus, in a loss-less cavity (infinite Q), an electromagnetic field can only be set up when its frequency is exactly equal to that given by (4.10); then the corresponding wavelengths in the three directions x, y, and z are given by

$$\lambda_x = \frac{2\pi}{k_x} = \frac{2a_x}{l}$$
$$\lambda_y = \frac{2\pi}{k_y} = \frac{2a_y}{m} \qquad (4.11)$$
$$\lambda_z = \frac{2\pi}{k_z} = \frac{2a_z}{n}$$

If there is any symmetry in the geometrical shape of the cavity (e.g., $a_x = a_y$), some modes may be characterized by the same value of ω; such modes are called *degenerate*.

4.2. Definition of a stationary state

Let us now return to quantum mechanics, limiting ourselves for the time being to conservative systems, in which the total energy of the

THE STATIONARY STATE

particle remains constant.[1] Then the potential V appearing in the Schrödinger equation no longer depends on time and (3.22) of chapter 3 can be written as

$$jh \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(\mathbf{r})\Psi \tag{4.12}$$

Equations of the type (4.12) are, in general, very difficult to solve but, fortunately, in many practical problems we can separate the variables by writing

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\psi_t(t) \tag{4.13}$$

Substituting this in (4.12) and introducing a separation constant, say, E, we obtain the following differential equation for the time-dependent function $\psi_t(t)$

$$\frac{\mathrm{d}\psi_t(t)}{\mathrm{d}t} = -\frac{j}{\hbar} E\psi_t(t) \tag{4.14}$$

Its solution is given by

$$\psi_t(t) = \mathrm{e}^{-jEt/\hbar} \tag{4.15}$$

so that (4.13) can now be written in the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, \mathrm{e}^{-jEt/\hbar} \tag{4.16}$$

We may note that, when multiplied by $\psi(\mathbf{r})$, equation (4.14) becomes the eigenvalue equation of the Hamiltonian operator $\hat{H}$, (3.65a). Substituting (4.16) in (4.12) we find that the time-independent part $\psi(\mathbf{r})$ of the wave function $\Psi(\mathbf{r}, t)$ must satisfy a differential equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi = E\psi \tag{4.17}$$

which is called the *time-independent* Schrödinger wave equation, since the time variable t does not appear in it either explicitly or implicitly. The separation of variables indicated by (4.13) has one important consequence: it is clear from (4.16) that now the probability density function $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) = \psi^*(\mathbf{r})\psi(\mathbf{r})$ and is independent of time so that the whole system, by definition, must not evolve with time. In general, when a system is in a state represented by a wave function of the type (4.16) it is said in quantum mechanics to be in a *stationary state* of energy E, as is the case for a non-radiating particle. Then, for brevity, $\psi(\mathbf{r})$ alone, rather than $\Psi(\mathbf{r}, t)$ may be referred to as the corresponding 'wave function'.

Comparison of (4.17) and (3.60a) shows that the separation constant E in (4.14) represents the total energy of the particle, as the letter chosen for it might imply. Furthermore, as we shall see shortly, if the particle is bound, the solutions of (4.17), i.e., the eigenfunctions $\psi(\mathbf{r})$ can only exist

for discrete energy eigenvalues E_n (or ω_n, by (3.9)). This means that, unlike a free particle which is associated with a wave packet a bound particle, when in a stationary state, must be associated with a single standing wave of a well-defined frequency ν. (However, since (4.17) is linear the superposition of several such solutions is possible and may lead to non-stationary states of a bound particle, as shown in chapter 5.) When the energy E is equal to one of its eigenvalues E_n, the corresponding standard deviation (see appendix 3) $\Delta E = 0$ and then, according to the uncertainty principle, (3.45), an infinite time interval Δt is required to measure the value of E. The physical meaning of this mathematical statement is that a stationary state does not lend itself to any kind of observation since the mere act of measurement is bound to introduce some alteration in the system and thus destroy the basic assumption of time independence. Since, in general, only transitions from one stationary state to another can be observed and not the states themselves, the experimental proof of their existence must be indirect, but they represent a very convenient, if somewhat idealized concept and their theory plays an important role in quantum mechanics.

4.3. Particle in an infinitely deep potential well

Let us now consider the simplest possible stationary state, viz., that of a particle contained in a three-dimensional potential well which is infinitely deep, i.e., a 'box' in which the potential V is zero inside and infinite everywhere outside. The time-independent wave function $\psi(\mathbf{r})$ must satisfy, inside the well, the following differential equation, which is obtained by putting $V = 0$ in (4.17),

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E\psi = 0 \qquad (4.18)$$

This equation strongly resembles (4.2) although the physical meaning of the two functions f and ψ is quite different, f representing the amplitude of a component of the electromagnetic field and ψ representing the amplitude of a matter wave. Putting $\beta = k$ in (3.11) we can write (4.18) in the form

$$\nabla^2 \psi + k^2 \psi = 0 \qquad (4.19)$$

where

$$k^2 \equiv \left(\frac{\omega}{v_p}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2 = \frac{2mE}{\hbar^2} = \frac{2m\omega}{\hbar} \qquad (4.20)$$

the particle behaving as a free particle ($V = 0$) within the confines of the box, in agreement with (3.9) and (3.5a) and showing the usual parabolic ω–k relation.

If the potential box in which the particle is contained has one corner

at the origin and has its respective edges of lengths a_x, a_y, and a_z along
the x-, y-, and z-axes, Fig. 4.1, the wave function must satisfy the following
boundary conditions

$$\psi = 0 \quad \text{at} \quad x = 0, \quad x = a_x$$
$$y = 0, \quad y = a_y \qquad (4.21)$$
$$z = 0, \quad z = a_z$$

The following physical meaning can be attached to these boundary con-
ditions. Since $V = 0$ inside the box and $V \to \infty$ everywhere else, the
probability of finding the particle outside the box must be zero; further-
more, since ψ must be continuous, $\psi = 0$ everywhere outside the box
and up to its walls, as shown in (4.21). Needless to say such boundary
conditions can never be satisfied in practice, since they would lead to a
discontinuity of slope all round the edges of the potential well; according
to (3.55) this, in turn, would require an infinite force acting along the
edges, a situation which is not realizable physically.

Comparing (4.19), (4.21) and (4.2), (4.4) we can immediately write
down the solution of (4.19) in the form

$$\psi_{lmn} = B_x B_y B_z \sin \frac{l\pi}{a_x} x \sin \frac{m\pi}{a_y} y \sin \frac{n\pi}{a_z} z \qquad (4.22)$$

or

$$\psi_{lmn} = \left(\frac{8}{a_x a_y a_z}\right)^{\frac{1}{2}} \sin \frac{l\pi}{a_x} x \sin \frac{m\pi}{a_y} y \sin \frac{n\pi}{a_z} z \qquad (4.22a)$$

after normalization, ψ_{lmn} being the eigenfunctions. Also, similarly to
(4.10), we now obtain from (4.20) an expression for the eigenvalues of
(4.19)

$$E_{lmn} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left\{\left(\frac{l\pi}{a_x}\right)^2 + \left(\frac{m\pi}{a_y}\right)^2 + \left(\frac{n\pi}{a_z}\right)^2\right\} \qquad (4.23)$$

As was to be expected, (4.23) shows that there are only certain values of
ω or E for which solutions of the Schrödinger equation (4.18) exist. Thus
a particle in a stationary state can only exist in the eigenstates E_{lmn} given
by (4.23), the corresponding eigenfunctions being given by (4.22). It
should be noted that the only formal difference between (4.3), commonly
used in electrical engineering, and (4.20) which applies to quantum
mechanics is that in the latter case the phase velocity v_p, entering into the
definition of the phase constant k, strongly depends on the frequency ω,
as has already been shown in section 3.2; in the case of (4.2) v_p is indepen-
dent of ω. Even this difference disappears if the medium is dispersive,
e.g., in the case of a plasma-filled cavity. Thus there is a close formal
similarity between the time-independent Schrödinger equation with

$V=0$ and the corresponding electromagnetic equation, but it should be noted that this analogy cannot readily be extended to the more general time-dependent equations.

Let us now calculate the mean energy, position, and momentum of a particle contained in an infinitely deep potential well. Starting with the mean energy, we obtain from (3.58) and (3.59) and the general expression for a wave function (4.16)

$$\langle E \rangle = j\hbar \int \Psi^*_{lmn} \frac{\partial}{\partial t} \Psi_{lmn} \, d\mathbf{r}$$

$$= j\hbar \int \Psi^*_{lmn} \left(-\frac{j}{\hbar} E_{lmn} \right) \Psi_{lmn} \, d\mathbf{r}$$

$$= E_{lmn} \int \Psi^*_{lmn} \Psi_{lmn} \, d\mathbf{r}$$

$$= E_{lmn} \tag{4.24}$$

which is in agreement with the assumption that the particle is in an energy eigenstate E_{lmn}, so that the standard deviation $\sigma_E = 0$.

It is instructive to calculate the numerical values of the differences between individual energy levels E_{lmn}. Since, according to (4.23), for a potential box which is in the form of a cube the typical difference between neighbouring low energy eigenvalues is given by $3(\hbar^2/2m)(\pi/a)^2$, we find that even for such small values as $m = 10^{-6}$ kg and $a = 10^{-3}$ m, this quantity is of the order of 10^{-55} joules or 10^{-36} eV. It is only for atomic particles, such as electrons ($m = 9 \cdot 11 \times 10^{-31}$ kg) and for atomic distances (e.g., $a = 1$ Å) that the differences in energy levels become significant and of the order of a few electron volts or more. For larger particles or distances the eigenvalues E_{lmn} become indistinguishable from a continuous set and then, in accordance with the correspondence principle, the laws of quantum mechanics go smoothly into those of classical mechanics. On the whole the energy eigenvalues get closer and closer together as the mass of the particle or the size of the box increases.

Now consider the mean position of the particle. From (3.52) we find that

$$\langle x \rangle = \int \Psi^*_{lmn} x \Psi_{lmn} \, d\mathbf{r}$$

$$= \frac{2}{a_x} \int_0^{a_x} x \sin^2 \frac{l\pi}{a_x} x \, dx$$

$$= \frac{2a_x}{l^2\pi^2} \int_0^{l\pi} \frac{l\pi}{a_x} x \sin^2 \frac{l\pi}{a_x} x \, d\left(\frac{l\pi}{a_x} x \right)$$

$$= \frac{2a_x}{l^2\pi^2} \tfrac{1}{4} l^2 \pi^2 = \tfrac{1}{2} a_x \tag{4.25}$$

5

Similarly, $y = \frac{1}{2}a_y$ and $z = \frac{1}{2}a_z$, so that we obtain in vector notation

$$\langle \mathbf{r} \rangle = \frac{1}{2}\mathbf{a} \tag{4.25}$$

Thus, the most likely position of the particle is in the middle of the potential box, irrespective of the value of E_{lmn}. The standard deviation σ_r is now greater than zero, as would be expected from the fact that the corresponding probability density function is continuous and given by

$$\Psi^*_{lmn}\Psi_{lmn} = \frac{8}{a_x a_y a_z} \sin^2 \frac{l\pi}{a_x} x \, \sin^2 \frac{m\pi}{a_y} y \, \sin^2 \frac{n\pi}{a_z} z \tag{4.26}$$

The probability density function (4.26) is shown in Fig. 4.2 for $l = m = n = 1$.
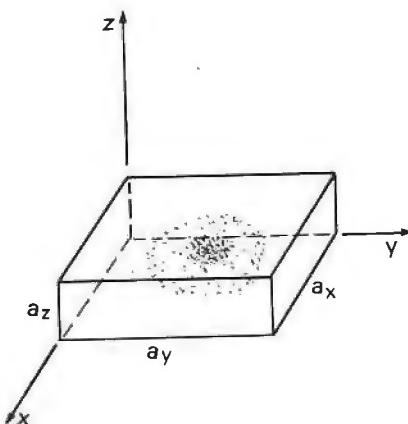
Fig. 4.2. Probability density function $\Psi^*\Psi$ for a particle inside an infinitely deep potential well, $l = m = n = 1$.

Finally, from (3.55) we can obtain the following expression for the mean value of the x component of the linear momentum of the particle

$$\langle p_x \rangle = -j\hbar \int \Psi^*_{lmn} \frac{\partial}{\partial x} \Psi_{lmn} \, d\mathbf{r}$$

$$= -j\hbar \frac{2}{a_x} \int_0^{a_x} \frac{l\pi}{a_x} \sin \frac{l\pi}{a_x} x \, \cos \frac{l\pi}{a_x} x \, dx$$

$$= 0 \tag{4.27}$$

Similarly, for the other two components, $\langle p_y \rangle = \langle p_z \rangle = 0$ or, in vector notation

$$\langle \mathbf{p} \rangle = 0 \tag{4.27}$$

Again, in agreement with what one might consider to be ordinary common sense, the mean linear momentum of a particle enclosed in a

zero potential box is shown to be zero. Of course, $\langle \mathbf{p} \rangle$ could have been calculated using the probability density function A^*A, as indicated by (3.19) and (3.53). In our case of discrete ω this function is simply given by

$$A(\mathbf{k}) = \pm \frac{j}{\sqrt{6}} \quad \text{or} \quad A^*(\mathbf{k})A(\mathbf{k}) = \tfrac{1}{6}$$

$$\text{at} \quad \mathbf{k} = \left(\pm \frac{l\pi}{a_x}, \pm \frac{m\pi}{a_y}, \pm \frac{n\pi}{a_z} \right) \tag{4.28}$$

and is shown in Fig. 4.3 (see also problems 12 and 13). Although from (4.22) and (4.23), to each eigenfunction Ψ_{lmn} there corresponds a single value of the phase constant k^2, the individual components of $\mathbf{k}$ can be either positive or negative, both directions of movement of the particle being equally likely.
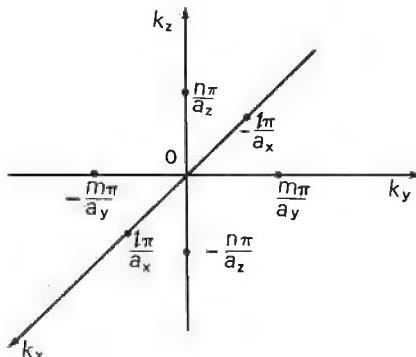
Fig. 4.3. Probability distribution $A^*(\mathbf{k})A(\mathbf{k})$ for a particle inside an infinitely deep potential well; each dot represents $A^*A = \tfrac{1}{6}$.

4.4. Particle in a potential well of height V_1

Let us now remove the artificial assumption that the well is infinitely deep, at the same time considering a one-dimensional case only for simplicity. We then have the following boundary conditions shown in Fig. 4.4.

$$V(z) = 0 \quad \text{for} \quad -a_z \leqslant z \leqslant +a_z$$

$$V(z) = V_1 \quad \text{for} \quad z < -a_z, z > a_z \tag{4.29}$$

Assume that the total energy E of the particle can never exceed the height of the potential barrier V_1. For $-a_z \leqslant z \leqslant +a_z$ we have $V = 0$ and a one-dimensional equivalent of (4.18) is now valid, but outside the well we have to use (4.17) which now gives

$$\frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}(E - V_1)\psi = 0 \tag{4.30}$$

A suitable expression for the eigenfunctions inside the well can be written directly by inspection of (4.8) and (4.23), viz.,

$$\psi = A_0 \cos k_0 z + B_0 \sin k_0 z \qquad (4.31)$$

where

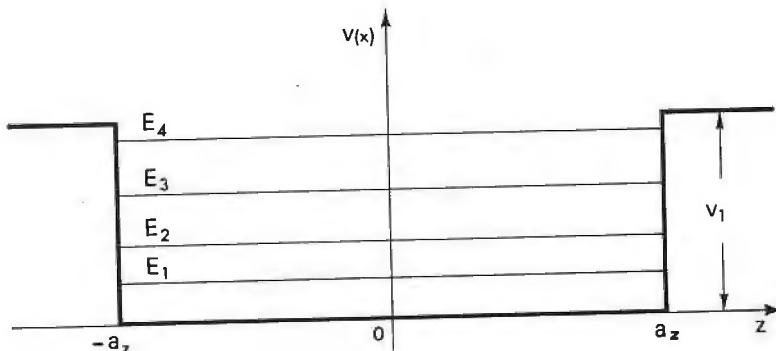$$k_0^2 = \frac{2mE}{\hbar^2} \qquad (4.32)$$

Fig. 4.4. Boundary conditions and energy levels for a particle inside a potential well of height V_1.

The situation is different, however, in the case of (4.30). Here $E - V_1 < 0$ so that outside the well the eigenfunctions must be non-periodic, giving

$$\psi = A_1 e^{-k_1 z} + B_1 e^{k_1 z} \qquad (4.33)$$

where

$$k_1^2 = \frac{2m(V_1 - E)}{\hbar^2} \qquad (4.34)$$

It is interesting to note that solutions (4.31) and (4.33) resemble similar expressions obtained for voltage or current distribution along loss-less, i.e., comprising L & C only, and purely resistive transmission lines, but here the analogy ends since in the case of a transmission line, the expressions equivalent to (4.18) or (4.30) are derived from a set of two first-order differential equations, whereas in the case of ψ-waves they are not. This affects the boundary conditions at the point where the two 'lines' join; in the electrical case both current and voltage must remain continuous, no restriction being placed on their slope, whereas in quantum mechanics ψ and $d\psi/dz$ must both be continuous.

Returning to (4.31) and (4.33) we find that since $\psi \to 0$ as $z \to \pm\infty$, $B_1 = 0$ for $z > 0$ and $A_1 = 0$ for $z < 0$. Also, as we have already said, at the edge of the potential well both the value and slope of the eigenfunctions

must be continuous. Substituting these conditions in (4.31) and (4.33) we obtain

$$B_0 = 0$$
$$\tan \frac{(2mE)^{\frac{1}{2}}}{\hbar} a_z = \left(\frac{V_1 - E}{E}\right)^{\frac{1}{2}} \qquad (4.35a)$$
$$A_1 = B_1$$

or

$$A_0 = 0$$
$$\cot \frac{(2mE)^{\frac{1}{2}}}{\hbar} a_z = -\left(\frac{V_1 - E}{E}\right)^{\frac{1}{2}} \qquad (4.35b)$$
$$A_1 = -B_1$$

Introducing, for convenience, the variables $\xi = a_z(2mE)^{\frac{1}{2}}/\hbar$ and $\eta = a_z\{2m(V_1 - E)\}^{\frac{1}{2}}/\hbar$, (4.35a) and (4.35b) become $\eta = \xi \tan \xi$ and $\eta = -\xi \cot \xi$,

(a)   (b)
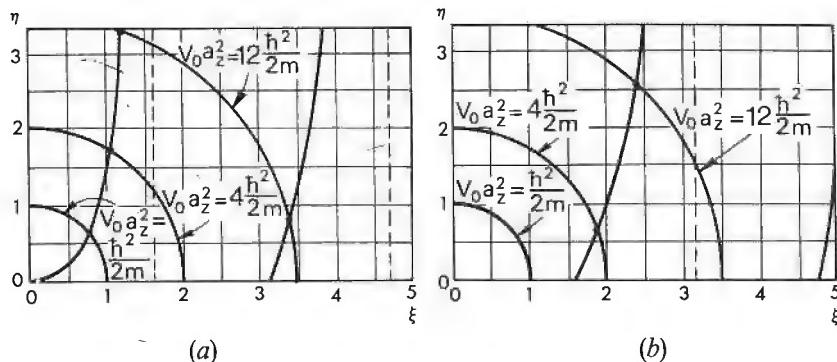
Fig. 4.5. Graphical solutions of (4.35a) and (4.35b); vertical dashed lines are the asymptotes. (From L. I. Schiff, *Quantum Mechanics*, 2nd ed., McGraw-Hill Book Company, New York, 1955.)

and are shown in Figs. 4.5a and b. Since $\xi^2 + \eta^2 = 2mV_1 a_z^2/\hbar^2$, a quantity which remains constant for any given system characterized by the mass of the particle and the dimensions of the potential well, the points where a given circle crosses the other family of curves correspond to the eigenstates of the system, each point being associated with a different value of the total energy of the particle, E_n. In very shallow or very narrow potential wells, when the values of $V_1 a_z^2$ are of the order of $\hbar^2/2m$ (for an electron $\hbar^2/2m = 3\cdot78 \times 10^{-20}$ eVm^2) only a few energy levels E_n are available to the particle, but as $V_1 a_z^2$ increases beyond atomic dimensions, the number of such energy levels grows rapidly, already being of the order of 10^3 for $V_1 = 1$ eV and $a_z = 1$ μ. Similarly, if the mass of the particle increases, the differences between individual values of E_n become

THE STATIONARY STATE

so small that the discrete system of energy levels can be safely approximated by a continuous one, the laws of classical mechanics becoming again applicable.

In Fig. 4.6 the eigenfunctions ψ are shown schematically for the first two eigenvalues E_n. For an infinitely deep well E_n would only depend on its width $2a_z$, as shown in (4.23), but for a well of finite depth, the eigenstates depend on both a_z and V_1. Furthermore, the reduction in the depth of the potential barrier from infinity to V_1 alters the boundary conditions in such a way that now the eigenfunction ψ is no longer zero at the edge of the potential well, but has a small non-zero value and then rapidly drops to zero as $z \to \pm\infty$. For example, in the case of an electron, k is of the order of 10^{10} m^{-1} for $E = 1$ eV, so that ψ becomes indistinguishable from zero at a distance of a few angstroms from the edge of the
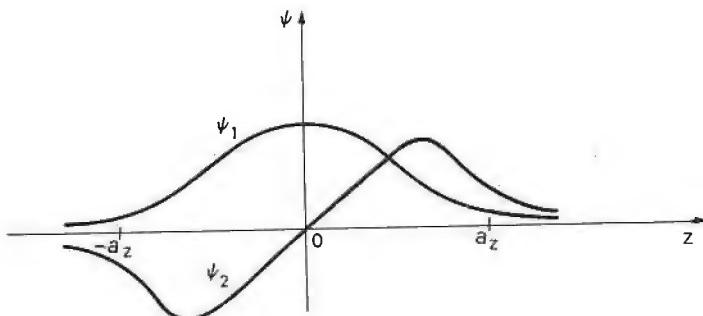
Fig. 4.6. The first two eigenfunctions of a particle contained in a potential well of height V_1; short vertical lines represent the edges of the well.

potential well. Here again we could calculate the mean position and momentum of the particle, as we did in section 4.3, but the labour involved would not be justified, except as an exercise, since the results would be in many respects similar to those discussed before. The main difference between the two systems resides in the fact that now the particle has a non-zero probability of finding itself outside the well, although its kinetic energy E is less than that required, according to classical mechanics, for scaling the potential barrier V_1. Such situations are quite contrary to the laws of classical mechanics and, since they occur in practice, their successful prediction has greatly added to the usefulness of quantum mechanics.

Let us now assume that instead of a single well, Fig. 4.4, we have two wells, side by side and separated by a thin potential barrier, as shown in Fig. 4.7. If we now solve (4.18) and (4.30) for the new set of boundary conditions, we discover that the wave function consists of an exponential rise at the edge of the first well, a periodic section of large amplitude across the first well, an exponential decay across the barrier, another
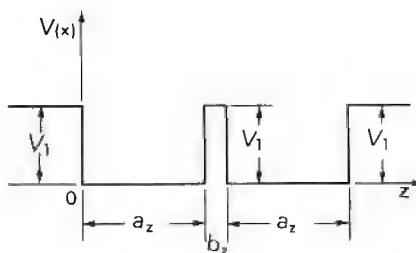
Fig. 4.7. Two neighbouring potential wells of height V_1 and width a_z, separated by a barrier of thickness b_z.

periodic section of small amplitude across the second well and finally an exponential decay to infinity, as shown in Fig. 4.8, assuming the particle is initially in the first well. (See also problem 16.) Since $\Psi^*\Psi$ is proportional to the probability of finding the particle at a given point in space, we can see that now the particle which is in a given energy state E_n, has a non-zero probability of finding itself in the second well in spite of the fact that its total energy E_n is less than the height of the potential barrier V_1. Thus in quantum mechanics the particle no longer has to be taken
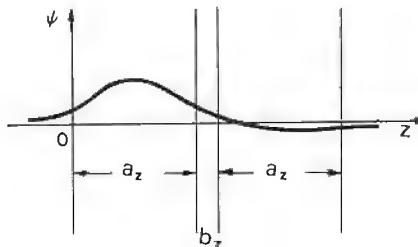
Fig. 4.8. The wave function ψ_1 for two neighbouring potential wells of height V_1 and width a_z.

over a potential barrier but it can 'tunnel' through it. Such a situation is quite foreign to the laws of classical mechanics and the discovery of its existence can be considered to be one of the great achievements of quantum mechanics. The experimental significance of the tunnel effect has been brought to the attention of electrical engineers with the discovery of the Esaki diode. An old example of tunnelling is the emission of electrons from cold bodies and the spontaneous emission of α-particles; more recent examples include the vibrations of a nitrogen atom in the ammonia maser and the operation of the so-called tunnel or cold cathodes.

The last problem to consider in connection with a particle in a potential well of depth V_1 is: what happens when the energy of the particle

$E > V_1$. Now the particle is no longer 'bound' (in the sense shown in Fig. 4.6) and the quantization of energy, which was imposed by the existing boundary conditions, is no longer required. The particle is now free and can have any energy we choose. Since an ideally free particle is a mathematical fiction however, we usually assume that the particle is still confined but in a second potential well which is very large and very deep compared to the first one. (See problem 17.) Although this reintroduces the quantization of the energy levels of the particle, now, because of the large size of the second well, they are so close together (see (4.23)), that the individual steps can be safely neglected and the energy distribution assumed to be virtually continuous.

4.5. Harmonic oscillator

So far we have been considering the behaviour of a particle in a potential well of constant depth. This was done largely in order to simplify the algebra of the problem, since the solution of even the time-independent Schrödinger equation (4.17) when $V = V(\mathbf{r})$ can be very difficult. To some extent this is comparable to the task of solving Maxwell's wave equation for inhomogeneous media, when ε and μ are functions of position. In fact, there are relatively few cases in quantum mechanics when the solution can be obtained in closed form: the harmonic oscillator and the hydrogen atom being two of them.

For the classical treatment of the harmonic oscillator, we start with the differential equation, which states that the acceleration is proportional to displacement

$$m\ddot{z} = -\kappa z \tag{4.36}$$

and obtain solutions in the form

$$z = A \cos \omega_c t + B \sin \omega_c t \tag{4.37}$$

where

$$\omega_c = \left(\frac{\kappa}{m}\right)^{\frac{1}{2}} \tag{4.38}$$

the constants A and B depending on the value of z and $\dot{z}$ at $t=0$. Practical examples of such oscillators are easily found in all branches of physics and engineering, the most common of them in electrical engineering being oscillatory circuits, when $z = q$(charge), $m = L$ and $\kappa = 1/C$ and oscillating dipoles, when the potential well is assumed to be parabolic, so that $V = \frac{1}{2}\kappa z^2$, giving the usual restoring force equal to $F = -\mathrm{d}V/\mathrm{d}z = -\kappa z$; for an electric dipole this force would be given by the electric charge times the electric field strength, similar expressions being valid for the magnetic dipole.

Let us now reconsider the whole problem in terms of quantum

mechanics, using Schrödinger's equation as a starting point. Putting $V = \frac{1}{2}\kappa z^2$ in the one-dimensional form of (4.17) we obtain

$$\frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}(E - \tfrac{1}{2}\kappa z^2)\psi = 0 \tag{4.39}$$

It is now convenient to rewrite (4.39) in terms of dimensionless variables. Putting $\zeta = \alpha z$, where $\alpha = (m\kappa/\hbar^2)^{\frac{1}{4}}$ and $\gamma = (2E/\hbar)(m/\kappa)^{\frac{1}{2}} = 2E/\hbar\omega_c$ where ω_c is given by (4.38), we obtain

$$\frac{d^2\psi}{dz^2} + (\gamma - \zeta^2)\psi = 0 \tag{4.40}$$

We can see from (4.40) that for large ζ the γ term can be neglected. Thus, the asymptotic solution of (4.40) must be of the form $\exp(-\frac{1}{2}\zeta^2)$, the positive sign in the exponential being excluded in view of the boundary condition $\psi \to 0$, as $\zeta \to \pm\infty$ required by normalization. The complete solution can now be written in the form

$$\psi = H(\zeta)\, e^{-\frac{1}{2}\zeta^2} \tag{4.41}$$

Substituting (4.41) in (4.40) we obtain a new differential equation for $H(\zeta)$, viz.,

$$H'' - 2\zeta H' + (\gamma - 1)H = 0 \tag{4.42}$$

where primes indicate differentiations with respect to ζ. Fortunately (4.42) is a known differential equation, the solution of which can be either a Hermite polynomial or a Hermite function, depending on whether γ is or is not an integer of the form $\gamma = 2n + 1$. It can be shown[2,3,4] that to satisfy the normalization condition the solution of (4.42) must be a Hermite polynomial H_n. The first few of these are as follows,

$$
\begin{aligned}
H_0 &= 1 & H_3 &= 8\zeta^3 - 12\zeta \\
H_1 &= 2\zeta & H_4 &= 16\zeta^4 - 48\zeta^2 + 12 \\
H_2 &= 4\zeta^2 - 2 & H_5 &= 32\zeta^5 - 160\zeta^3 + 120\zeta
\end{aligned}
\tag{4.43}
$$

the general expression being of the form

$$H_n(\zeta) = (-1)^n\, e^{\zeta^2}\, \frac{d^n}{d\zeta^n}\, e^{-\zeta^2} \tag{4.44}$$

Substituting back in (4.41) we find that the eigenfunctions have the following general form

$$
\begin{aligned}
\psi_n &= A_n H_n(\zeta)\, e^{-\frac{1}{2}\zeta^2} \\
&= A_n H_n(\alpha z)\, e^{-\frac{1}{2}\alpha^2 z^2}
\end{aligned}
\tag{4.45}
$$

where the normalization constant is given by

$$A_n = \left(\frac{\alpha}{2^n n! \pi^{\frac{1}{2}}}\right)^{\frac{1}{4}} \tag{4.46}$$

its calculation requiring additional theorems on the integrals of $H_n(\zeta)$.[2,3] However, the energy eigenvalues can be calculated directly from the definition of γ, and from the condition imposed on it to make $H(\zeta)$ a polynomial:

$$E_n = \tfrac{1}{2}\hbar\omega_c\gamma = (n+\tfrac{1}{2})\hbar\omega_c \tag{4.47}$$

We make here two important observations: since $V = V(\zeta)$, the linear momentum of the particle also depends on ζ and we can no longer associate a single wavelength λ with the particle; secondly, for a parabolic potential well the energy eigenvalues E_n are equally spaced, the difference between any two neighbouring values being exactly equal to $\hbar\omega_c = h\nu_c$, as required to conform with the ideas of Planck and Einstein,[5,6] discussed in chapter 2.

The eigenvalues ψ_n for the first six values of n and the probability density function $\psi^*\psi$ for $n = 10$ are respectively shown in Figs. 4.9 and 4.10. The horizontal line in Fig. 4.9 shows in each case the amplitude of oscillation of the corresponding classical oscillator of total energy E_n,
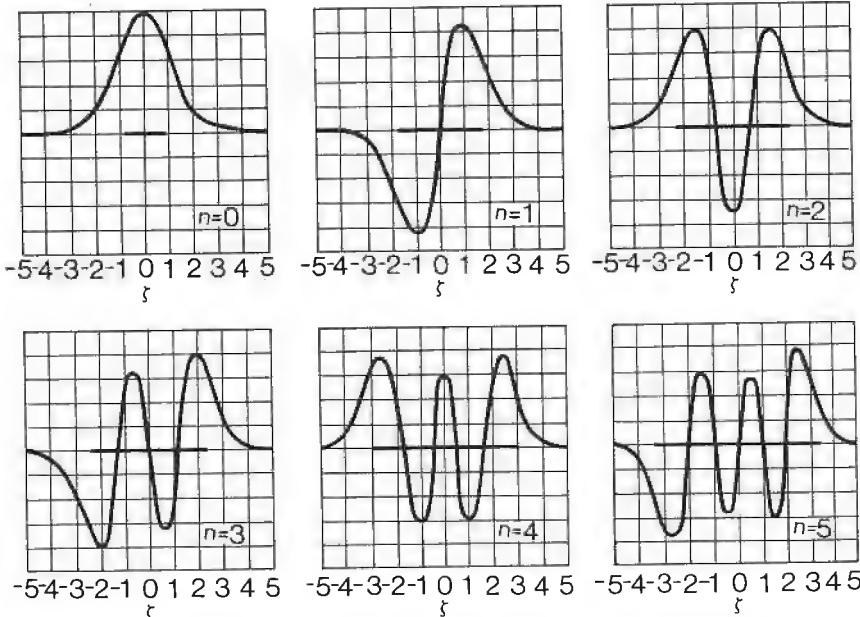
Fig. 4.9. The time-independent part of the wave function ψ of a harmonic oscillator for the first six values of n. (From L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Company, New York, 1935.)

derived from the usual considerations of zero kinetic energy and maximum potential energy at the point of maximum excursion. The dotted curve in Fig. 4.10 shows the classical probability density function for the position of the particle given by

$$f(\zeta) = \frac{1}{\pi(\zeta_0^2 - \zeta^2)^{\frac{1}{2}}} \tag{4.48}$$

where ζ_0 is the amplitude of the classical oscillator whose energy is equal to E_{10} (see also problem 18). Figure 4.10 clearly shows that, in accordance
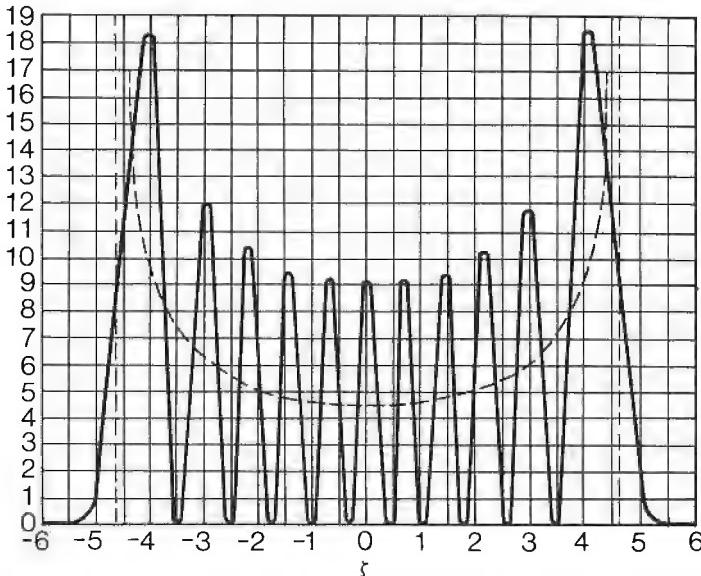

Fig. 4.10. The probability density function $\Psi^*\Psi$ of a harmonic oscillator in the energy state $n = 10$. (From L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Company, New York, 1935.)

with the correspondence principle, the behaviour of the harmonic oscillator rapidly approaches that of its classical counterpart as n increases. Finally, one should add that from (4.16), (4.45), and (4.47) the time-dependent form of the wave function is given by

$$\Psi_n(z, t) = \left(\frac{\alpha}{2^n n! \pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} H_n(\alpha z) \, e^{-\frac{1}{2}\alpha^2 z^2} \, e^{-j(n+\frac{1}{2})\omega_c t} \tag{4.49}$$

ω_c being the corresponding frequency of a classical oscillator.

The concept of a harmonic oscillator was of great importance in the historical development of quantum mechanics. Furthermore, according to (4.47), the lowest energy that a harmonic oscillator can have is $E_0 = \frac{1}{2}\hbar\omega_c$ and not zero, as would be expected on the basis of classical mechanics and

there is, therefore, a certain energy density associated with electromagnetic radiation even at zero temperature, which appears as noise, the so-called quantum noise, which is quite distinct from the Johnson noise of a resistor or the thermal noise of an electron beam. Although in view of the smallness of $\hbar$ this noise is negligibly small at lower frequencies, it begins to play its part at submillimetre wavelengths and becomes of paramount significance in lasers, which operate at optical frequencies. These considerations can also be used to explain Einstein's postulate that spontaneous atomic transitions can only take place downwards and never upwards.[7]

Let us now calculate the mean value of the total energy E, potential energy V, position z, and linear momentum p of a particle subjected to a harmonic restoring force. To avoid undue algebraic complications we will carry out these calculations only for the ground state $n=0$, where from (4.49)

$$\Psi_0(z, t) = \left(\frac{\alpha}{\pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\alpha^2 z^2} e^{-j\frac{1}{2}\omega_c t} \tag{4.50}$$

the more general calculations being available elsewhere.[2, 3] Using the common definition for the mean or expectation value of a quantity, we obtain for the mean value of the total energy

$$\langle E \rangle = j\hbar \int \Psi_0^* \frac{\partial}{\partial t} \Psi_0 \, dz$$

$$= j\hbar \int \Psi_0^*(-j\tfrac{1}{2}\omega_c)\Psi_0 \, dz$$

$$= \tfrac{1}{2}\omega_c\hbar = E_0 \tag{4.51}$$

$$\langle E^2 \rangle = -\hbar^2 \int \Psi_0^* \frac{\partial^2}{\partial t^2} \Psi_0 \, dz$$

$$= -\hbar^2 \int \Psi_0^*(-j\tfrac{1}{2}\omega_c)^2\Psi_0 \, dz$$

$$= (\tfrac{1}{2}\omega_c\hbar)^2 = E_0^2 \tag{4.52}$$

As was to be expected, the total energy of the particle E is equal to the eigenvalue E_0, the square of the standard deviation being zero, $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = 0$.

The mean potential energy of the particle in the lowest or ground state is given by

$$\langle V \rangle = \int \Psi_0^* V \Psi_0 \, dz$$

$$= \frac{\alpha}{\pi^{\frac{1}{2}}} \int \tfrac{1}{2} \kappa z^2 \, e^{-\alpha^2 z^2} \, dz$$

$$= \frac{\kappa}{4\alpha^2}$$

$$= \tfrac{1}{2}\hbar \left(\frac{\kappa}{m}\right)^{\frac{1}{2}} = \tfrac{1}{4}\omega_c \hbar = \tfrac{1}{2}E_0 \qquad (4.53)$$

which is exactly half its total energy, in agreement with the results obtained in classical mechanics, the remainder being equal to the mean kinetic energy, as we shall see shortly.

The other important quantities, viz., $\langle z \rangle$, $\langle z^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$ can now be calculated without too much difficulty

$$\langle z \rangle = \int \Psi_0^* z \Psi_0 \, dz$$

$$= \frac{\alpha}{\pi^{\frac{1}{2}}} \int z \, e^{-\alpha^2 z^2} \, dz$$

$$= 0 \qquad (4.54)$$

$$\langle z^2 \rangle = \frac{\alpha}{\pi^{\frac{1}{2}}} \int z^2 \, e^{-\alpha^2 z^2} \, dz$$

$$= \frac{1}{2\alpha^2} \qquad (4.55)$$

$$\langle p \rangle = -j\hbar \int \Psi_0^* \frac{\partial}{\partial z} \Psi_0 \, dz$$

$$= j\hbar \frac{\alpha^3}{\pi^{\frac{1}{2}}} \int z \, e^{-\alpha^2 z^2} \, dz$$

$$= 0 \qquad (4.56)$$

$$\langle p^2 \rangle = -\hbar^2 \int \Psi_0^* \frac{\partial^2}{\partial z^2} \Psi_0 \, dz$$

$$= \hbar^2 \frac{\alpha}{\pi^{\frac{1}{2}}} \int (\alpha^2 - \alpha^4 z^2) \, e^{-\alpha^2 z^2} \, dz$$

$$= \tfrac{1}{2}\alpha^2 \hbar^2 \qquad (4.57)$$

Since the mean kinetic energy can be written, in view of Ehrenfest's theorem, (3.79), as

$$\langle T \rangle = \frac{\langle p^2 \rangle}{2m} \qquad (4.58)$$

we obtain, by substituting (4.57) in (4.58)

$$\langle T \rangle = \frac{\alpha^2 \hbar^2}{4m}$$

$$= \tfrac{1}{4}\hbar \left(\frac{\kappa}{m}\right)^{\frac{1}{2}}$$

$$= \tfrac{1}{4}\omega_c\hbar = \tfrac{1}{2}E_0 \tag{4.59}$$

in agreement with the comments made previously in connection with (4.53). It should be noted that the probability distribution used for calculating $\langle z \rangle$, $\langle z^2 \rangle$, and $\langle V \rangle$ is continuous, its standard deviation being different from zero, unlike the corresponding probability distribution for E which comprises a single point $E = E_0$. Since both $\langle z \rangle$ and $\langle p \rangle$ are zero, in agreement with our macroscopic or classical approach to the harmonic oscillator, we can write directly from (4.55) and (4.57)

$$\sigma_z \sigma_p = (\langle z^2 \rangle \langle p^2 \rangle)^{\frac{1}{2}} = \tfrac{1}{2}\hbar \tag{4.60}$$

This is a particular example of the general expression for the uncertainty principle (3.39) derived in chapter 3, where σ_z and σ_p are written Δz and Δp. It can be shown, using higher order eigenfunctions Ψ_n in place of Ψ_0 that, in general,[2,3]

$$\sigma_z \sigma_p = (n + \tfrac{1}{2})\hbar \tag{4.60a}$$

so that (4.60) represents the minimum value of the product and, being of the order $\hbar$, agrees with the general theory which places a limit on the joint accuracy of simultaneous measurement of z and p.

It should be added, for the sake of completeness, that the other component of the Fourier pair, (3.46a), i.e., the corresponding representation of the ground state in the **k**-(or β-)space can be obtained by substituting (4.50) in (3.46a). This gives

$$A_0(\beta) = \frac{e^{j\omega t}}{(2\pi)^{\frac{1}{2}}} \int \Psi_0(z, t) \, e^{-j\beta z} \, dz$$

$$= \frac{1}{(\alpha\pi^{\frac{1}{2}})^{\frac{1}{2}}} \, e^{-\beta^2/2\alpha^2} \tag{4.61}$$

since in this case $\omega = \tfrac{1}{2}\omega_c = E/\hbar$. The corresponding probability density function of the variable β and, thus, of the linear momentum of the particle is given by

$$A_0^* A_0 = \frac{1}{\alpha\pi^{\frac{1}{2}}} \, e^{-\beta^2/\alpha^2} \tag{4.62}$$

which can be used directly for calculating $\langle p \rangle$ and $\langle p^2 \rangle$ (see problem 20).

Finally, it should be pointed out that, unless the particle is of atomic

dimensions, leading, from (4.38), to an extremely high value of ω_c, the differences $\hbar\omega_c$ between individual energy levels of the system are quite negligible and the usual approximation of classical mechanics, i.e., a continuous distribution of energy is quite adequate. For example, a particle of mass $m = 10^{-6}$ kg vibrating at $v_c = 100$ c/s with an amplitude $z_a = 10^{-4}$ m is in an energy state of the order $n = 10^{22}$, the differences in energy between neighbouring eigenstates being given by $hv_c = 6\cdot6 \times 10^{-32}$ joules or $4\cdot1 \times 10^{-13}$ eV.

4.6. The hydrogen atom

Let us now consider another case for which solutions of the time-independent Schrödinger equation with $V = V(r)$ are known in a closed form, viz., the hydrogen atom. Here a single electron carrying a negative charge $-e$ is bound to a positive proton of charge $+e$, the potential function describing the electric field surrounding the nucleus being of the form $V(r) = -e^2/4\pi\varepsilon_0 r$. Here r stands for the distance between the charges and ε_0 has the usual value of the dielectric constant of vacuum. The symmetry properties of the potential function V suggest that we should use in this case the spherical polar coordinates (r, θ, ϕ), Fig. 4.11, in preference to the more common cartesian coordinates (x, y, z).
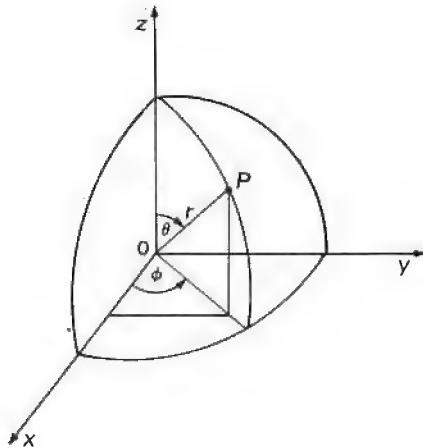
Fig. 4.11. The spherical polar coordinates (r, θ, ϕ) of a point P.

Expressing the Laplacian of (4.17) in terms of the new coordinates we obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+ \frac{1}{r^2\sin\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}\{E - V(r)\}\psi = 0 \qquad (4.63)$$

where m stands for the mass of an electron. However, (4.63) would be true, strictly speaking, only if the nucleus of the atom, i.e., the proton, were infinitely heavy. In reality it is not, the ratio of the two masses being equal to 1836. This means that the two particles move relative to a common centre of gravity and in place of $m = m_e$ in (4.63) we should use the reduced mass $m = m_e m_p / (m_e + m_p)$ as explained in appendix 4, m_e and m_p respectively standing for the mass of electron and proton.

Similarly to (4.5) and (4.22) we now postulate a solution of the form

$$\psi = R(r)\Theta(\theta)\Phi(\phi) \tag{4.64}$$

where each constituent function depends on a single variable only. Substituting (4.64) in (4.63) we obtain a set of three ordinary differential equations. The simplest of them contains the function Φ,

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \tag{4.65}$$

Its solutions are given by

$$\Phi_m(\phi) = A_\phi\, e^{jm\phi} \qquad m = 0, \pm 1, \pm 2, \ldots \tag{4.66}$$
$$= (2\pi)^{-\frac{1}{2}}\, e^{jm\phi}$$

Here the constant m must be an integer to make the function Φ single valued.

The next differential equation in order of complexity is that for Θ. Putting $-m^2$ in place of the term depending on ϕ, we obtain from (4.63)

$$\frac{d^2\Theta}{d\theta^2} + \frac{1}{\tan\theta}\frac{d\Theta}{d\theta} + \left(-\frac{m^2}{\sin^2\theta} + l(l+1)\right)\Theta = 0 \tag{4.67}$$

This is the Legendre equation and its solution is given by[8,9]

$$\Theta_{lm} = A_\theta P_l^m(\cos\theta)$$
$$= \left(\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right)^{\frac{1}{2}} P_l^m(\cos\theta) \tag{4.68}$$

$$l = 0, 1, 2, \ldots, \quad m = 0, 1, 2, \ldots, l$$

where P_l^m are the associated Legendre functions of the first kind and A_θ is the usual normalization constant. (For simplicity, m in (4.68) stands for $|m|$ of (4.66), since in (4.67) only m^2 appears.) Suitable expressions for P_l^m for the first few values of l and m are given below

$$P_0^0 = 1, \qquad P_2^0 = \tfrac{1}{4}(3\cos 2\theta + 1)$$
$$P_1^0 = \cos\theta, \qquad P_2^1 = \tfrac{3}{2}\sin 2\theta$$
$$P_1^1 = \sin\theta, \qquad P_2^2 = \tfrac{3}{2}(1 - \cos 2\theta) \tag{4.69}$$

the corresponding normalized functions Θ_{lm} being shown in Fig. 4.12.

To keep the solutions of (4.67) finite everywhere, including the two poles of Fig. 4.11 for which $\cos \theta = \pm 1$, we must ignore the Legendre functions of the second kind $Q_l^m(\cos \theta)$; for the same reason l must be an integer greater than or equal to m. This latter condition can be better understood if we look at (4.67). For $m=0$, the only danger may be associated with the coefficient $1/\tan \theta$ which becomes infinite at $\theta = n\pi$; to counteract this, $d\Theta/d\theta$ must be zero at those points (see Fig. 4.12),
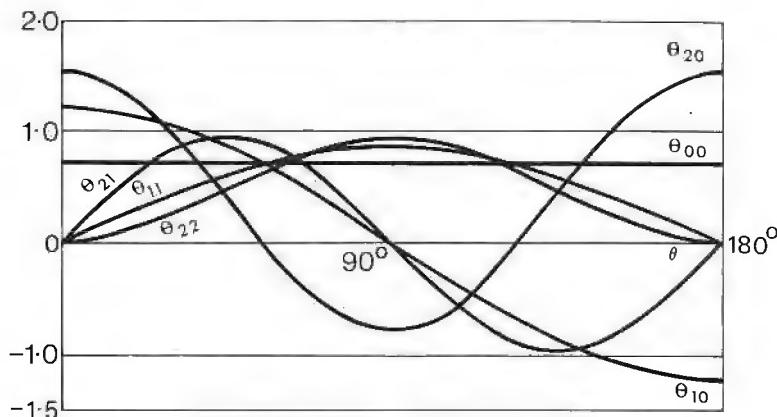
Fig. 4.12. The first few Θ_{lm} functions, which are the normalized associated Legendre functions of the first kind $A_\theta P_l^m(\cos \theta)$.

although no such restriction need be placed on the value of Θ itself. It can be further shown that the only P_l^m functions which satisfy this condition are those with positive integral values of l. If $m = \pm 1$, both coefficients, $1/\tan \theta$ and $1/\sin^2 \theta$, tend to infinity for $\theta = n\pi$; now we can show, by taking the first terms of the corresponding series expansions for $\tan \theta$ and $\sin \theta$ (see problem 24) that $\Theta = k\theta$ where k is the slope of Θ near the poles, keeps the function well behaved. This condition permits $P_1^1, P_2^1, \ldots, P_l^1$, but not P_0^1 since $l=0$ would make the solution bend the wrong way. Finally, we find from (4.67) that for higher values of m, both Θ and $d\Theta/d\theta$ must be equal to zero at the crucial points, $\theta = n\pi$ to suppress the singularities due to the two troublesome coefficients. Furthermore, if for any of those values of m we allowed the condition $m \leqslant l$ to be violated, the negative sign in front of the term containing m^2 would push the function to infinity at $\theta = n\pi$, as can be ascertained by writing (4.67) in the form of finite differences starting with $\Theta = 0$ or $d\Theta/d\theta = 0$ at $\theta = 90°$ for symmetry reasons (see problem 25).

The third differential equation which is obtained from (4.63) depends

6

on the radial distance r only

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2m}{\hbar^2}E+\frac{2m}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)}{r^2}\right)R=0 \qquad (4.70)$$

where an appropriate expression has been substituted for $V(\mathbf{r})$.

Let us now introduce two new constants:

$$a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{me^2} = 0\cdot529 \text{ Å} \qquad (4.71)$$

where m is the reduced electron mass for a hydrogen atom, and a new quantum number n, defined by

$$-\frac{1}{n^2 a_0^2} = \frac{2mE}{\hbar^2} \qquad (4.72)$$

the energy of a bound electron being essentially a negative quantity. In terms of the new constants, (4.70) reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2}{a_0 r}-\frac{1}{n^2 a_0^2}-\frac{l(l+1)}{r^2}\right)R=0 \qquad (4.73)$$

The solutions of (4.73) take the form

$$R_{nl}(r) = A_r r^l\, e^{-r/na_0} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$= \left(\frac{2}{na_0}\right)^{\frac{3}{2}}\left(\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right)^{\frac{1}{2}}\left(\frac{2r}{na_0}\right)^l e^{-r/na_0} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$= \alpha^{\frac{3}{2}}\left(\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right)^{\frac{1}{2}}\rho^l\, e^{-\frac{1}{2}\rho} L_{n-l-1}^{2l+1}(\rho) \qquad (4.74)$$

$$n = 1, 2, 3, \ldots, \quad l = 0, 1, \ldots, (n-1)$$

where L_{n-l-1}^{2l+1} are the associated Laguerre polynomials,[10] A_r is the usual normalization constant and $\rho = \alpha r$, $\alpha = 2/na_0$ is a new variable. In order to keep R_{nl} finite everywhere we must make n a positive integer greater than l, so that the largest allowed value of l is $n-1$; for the same reason the second solution of (4.73) containing r^{-l-1} cannot be allowed, since this term becomes infinite at the origin. The associated Laguerre polynomials for the first few values of n and l are given below

$$L_0^0 = 1, \quad L_0^1 = 1, \quad L_0^2 = 2, \quad L_0^k = k!$$

$$L_1^0 = 1-\rho, \quad L_1^1 = 4-2\rho,$$

$$L_1^2 = 18-6\rho, \quad L_1^3 = 96-24\rho$$

$$L_2^0 = 2-4\rho+\rho^2, \quad L_2^1 = 18-18\rho+3\rho^2,$$

$$L_2^2 = 144-96\rho+12\rho^2 \qquad (4.75)$$

The complete R_{nl} functions using some of the Laguerre polynomials given above are shown in Fig. 4.13, where a_0 and $a_0^{-\frac{3}{2}}$ respectively serve as natural units along the horizontal and vertical axes. We can see from (4.74) that all R_{nl} functions have the form of a triple product comprising the lth power of r, an exponential function of the form $\exp(-r/na_0)$ and an associated Laguerre polynomial $L_{n-l-1}^{2l+1}(2r/na_0)$ which is of order $n-l-1$ and thus has $n-l-1$ zeros between 0 and ∞. (Some authors use a different notation designating $L_{n-l-1}^{2l+1}(\rho)$ by $(-1)^{2l+1}L_{n+l}^{2l+1}(\rho)$.)
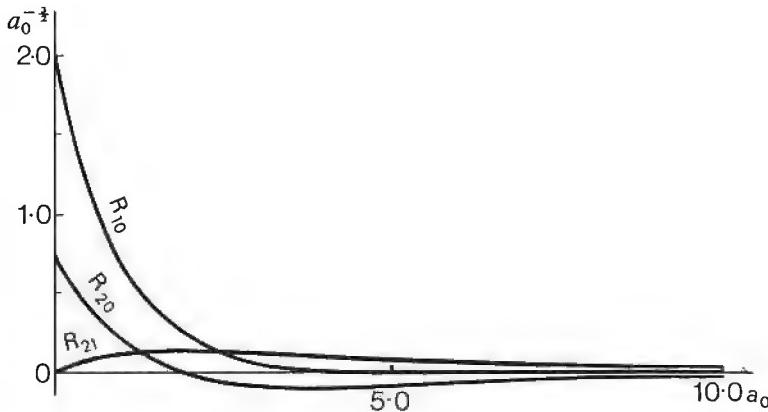
Fig. 4.13. The function R_{nl} for the first few values of n and l.

A complete solution of the wave equation (4.63) for a hydrogen atom can now be obtained by substituting (4.66), (4.68), and (4.74) in (4.64). This gives the following general expression for the time-independent part of the wave functions

$$\psi_{nlm} = A_r A_\theta A_\phi r^l \, e^{-r/na_0} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) P_l^m(\cos\theta)\, e^{jm\phi} \qquad (4.76)$$

where the last m can be either positive or negative. Substituting suitable values for the normalization constants A_r, A_θ, and A_ϕ we obtain the following expressions for the first five eigenfunctions of the system:

$$\Psi_{100} = a_0^{-\frac{3}{2}}\pi^{-\frac{1}{2}} \, e^{-r/a_0} \, e^{-jE_1 t/\hbar}$$

$$\Psi_{200} = \tfrac{1}{4}a_0^{-\frac{3}{2}}(2\pi)^{-\frac{1}{2}} \, e^{-r/2a_0}\left(2-\frac{r}{a_0}\right)e^{-jE_2 t/\hbar}$$

$$\Psi_{210} = \tfrac{1}{4}a_0^{-\frac{3}{2}}(2\pi)^{-\frac{1}{2}} \, e^{-r/2a_0}\frac{r}{a_0}\cos\theta \, e^{-jE_2 t/\hbar}$$

$$\Psi_{21\pm1} = \tfrac{1}{8}a_0^{-\frac{3}{2}}\pi^{-\frac{1}{2}} \, e^{-r/2a_0}\frac{r}{a_0}\sin\theta \, e^{\pm j\phi} \, e^{-jE_2 t/\hbar} \qquad (4.77)$$

Here the energy eigenvalues E_n are obtained from (4.72) which gives, after a suitable value has been substituted for a_0,

$$E_n = -\frac{me^4}{2n^2\hbar^2}\frac{1}{(4\pi\varepsilon_0)^2}$$

$$= -\frac{Ry}{n^2} \tag{4.78}$$

where $Ry = 2\cdot18 \times 10^{-18}$ joules or 13·6 eV is known as the Rydberg constant and has the dimensions of energy. (In spectroscopy, where the term originated, it is more usual to talk about the Rydberg number, i.e., the wave number, or 'improper frequency' given by $1/\lambda = \tilde{v} = Ry/hc = 109,737$ cm^{-1}.) A correct prediction of the eigenvalues (4.78) which agreed with the experimentally determined Rydberg number, constituted one of the first great victories of quantum mechanics.[11] The probability density function $\Psi^*\Psi = \psi^*\psi$ corresponding to the eigenfunctions quoted in (4.77) are shown in Fig. 4.14. They are functions of all three variables (r, θ, ϕ) and can only be shown with some difficulty, the depth of shading, for example, being made proportional to the value of the function.

It should be noted here that the functions (4.66) and (4.68) are the same as in the case of a spherical resonant cavity, though (4.74) is not. The difference in the r-dependent solution, apart from altered boundary conditions, is due to the fact that in the case of a spherical cavity the middle term in the brackets of (4.70) is missing and the first term is essentially positive. Thus, in place of (4.74) containing associated Laguerre polynomials, we have

$$R_{nl} = A_r\left(\frac{r}{na_0}\right)^{-\frac{1}{2}}Z_{l+\frac{1}{2}}\left(\frac{r}{na_0}\right) \tag{4.79}$$

where $Z_{l+\frac{1}{2}}$ is a half-order Bessel function. Here A_r depends on the total amount of electromagnetic energy stored in the cavity and a_0 relates to the cavity radius, since the metallic walls can only be placed at the wave nodes, i.e., at the zeros of the Bessel function $Z_{l+\frac{1}{2}}$.

Let us now consider the mean energy and position of an electron in the hydrogen atom. Since all the wave functions are of the form

$$\Psi_{nlm} = \psi_{nlm}\,e^{-jE_nt/\hbar} \tag{4.80}$$

the energy of the electron is equal to the corresponding eigenvalue, its mean value being given by

$$\langle E \rangle = j\hbar \int \Psi_{nlm}^*\frac{\partial}{\partial t}\Psi_{nlm}\,d\tau$$

$$= \int \Psi_{nlm}^*E_n\Psi_{nlm}\,d\tau$$

$$= E_n \tag{4.81}$$

Here the element of volume $d\tau$ is no longer $dr = dx\,dy\,dz$ but $d\tau = r^2 \sin\theta\,d\theta\,d\phi$.

Investigating the algebraic form of (4.76) we find that the mean position of the particle in the ϕ-direction is given by

$$\langle\phi\rangle = \int \Psi^*_{nlm}\phi\Psi_{nlm}\,d\tau$$

$$= \frac{1}{2\pi}\int_{\alpha}^{\alpha+2\pi} \phi\,d\phi = \alpha+\pi \tag{4.81a}$$

This can have any value depending on the choice of α. Since $\Psi^*\Psi$ is independent of ϕ, whatever the value of the quantum numbers n, l, m, it
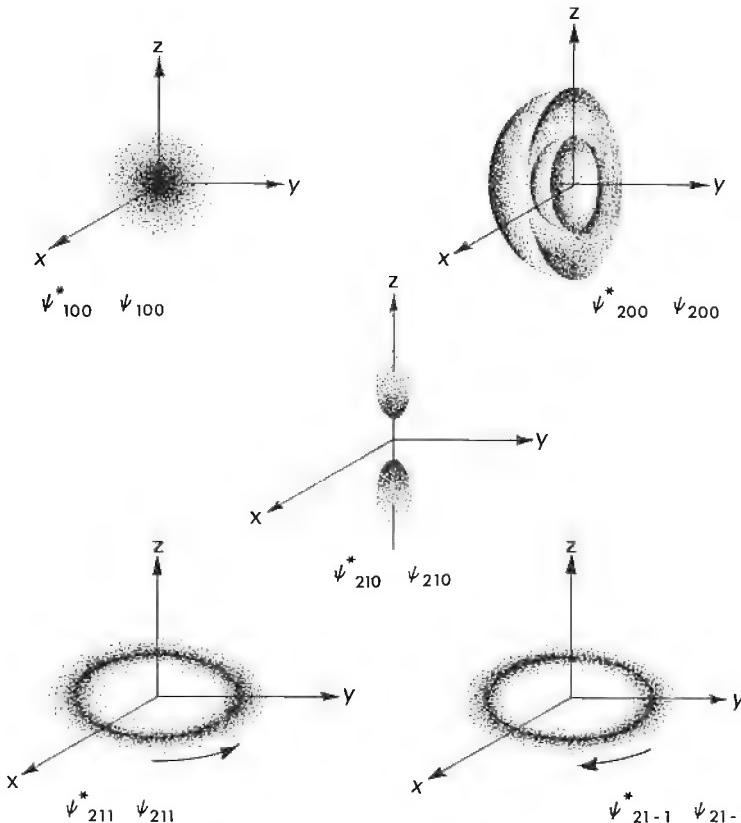
Fig. 4.14. Probability density function of the electron in a hydrogen atom for $n=1, 2$.

should not surprise us that there is no preferred value for the angle (see also Fig. 4.14). Carrying out similar calculations for the angle θ we find that as long as $l=0$, the same applies to $\langle\theta\rangle$; for other values of l, however, $\langle\theta\rangle=\frac{1}{2}\pi$, as can easily be deduced from the fact that the $\{P_l^m(\cos\theta)\}^2$

functions are symmetrical with respect to $\theta = \frac{1}{2}\pi$. Finally, let us calculate the mean radial position of the electron. Taking the ground state Ψ_{100} as an example, we find from (4.77) that

$$
\begin{aligned}
\langle r \rangle_{100} &= \int \Psi_{100}^* r \Psi_{100} \, d\tau \\
&= \int_0^\infty r^3 R_{10}^2 \, dr \\
&= \frac{1}{2\alpha} \int_0^\infty \rho^3 \, e^{-\rho} \, d\rho \\
&= \frac{1}{2\alpha} 3! \\
&= \frac{3}{2} a_0
\end{aligned}
\tag{4.82}
$$

It is of greater interest, however, to calculate the probability of finding an electron in a shell $(r, r + dr)$, whatever the value of θ or ϕ. The appropriate marginal probability density function (see appendix 3) is given by

$$
\begin{aligned}
f(r) &= \int_0^{2\pi} \int_0^\pi \Psi_{100}^* \Psi_{100} r^2 \sin\theta \, d\theta \, d\phi \\
&= r^2 R_{10}^2 \\
&= \frac{1}{a_0} \left(\frac{2r}{a_0} \right)^2 e^{-2r/a_0}
\end{aligned}
\tag{4.83}
$$

This function has a maximum at $r = a_0$, as shown in Fig. 4.15, so that the charge density for an electron in the ground state is highest at that point (note that $a_0 \neq \langle r \rangle_{100}$). The constant a_0 is sometimes referred to as the Bohr radius, since, according to the 'old' quantum mechanics, it corresponds to the radius of the smallest electron 'orbit'. The old quantum mechanics was developed by Bohr in a very successful attempt to explain the line structure of the hydrogen spectrum, before the more comprehensive theory due to Schrödinger and others was known.[12]

Let us now consider the physical meaning of the three quantum numbers n, l, m. First of all we note from (4.78) that the energy levels E_n depend on the quantum number n only. This is due to the assumption of pure Coulomb potential, $V = V(r) \propto 1/r$ so that n appears for the first time in (4.73). However, in practice, other interaction forces must also be considered and the value of E becomes dependent on the other two constants l and m, though to a smaller degree. Even so, (4.78) gives a very good insight into the long-standing mystery of the experimentally derived expressions for the calculation of Lyman, Balmer, Paschen, and other

line series discernible in the spectrum of atomic hydrogen. For example, in the case of the first two series we obtain from (4.78), as predicted,

$$E_n - E_1 = Ry\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \tag{4.84}$$

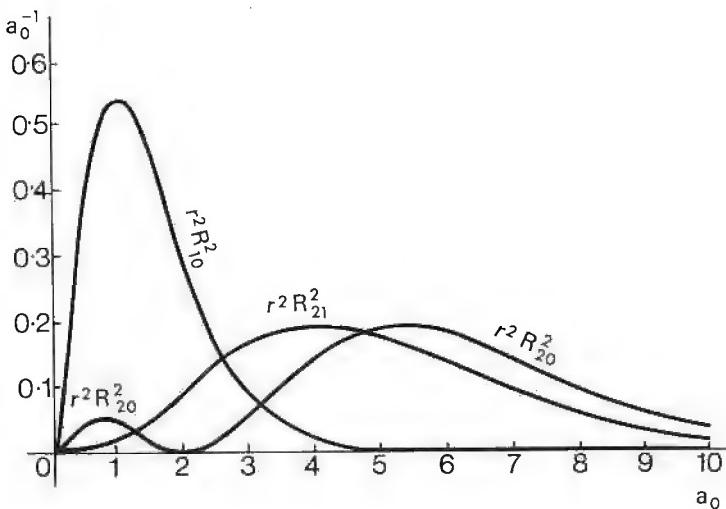$$E_n - E_2 = Ry\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{4.85}$$

Fig. 4.15. The radial distribution of space charge in a hydrogen atom given by $r^2 R_{nl}^2$.

Figure 4.16 shows schematically how the Lyman, Balmer, and Paschen series are in fact generated by electron transitions between different energy levels.

The set of integers n, l, m is so important in quantum mechanics that it is usual to refer to them by separate names. The first constant, n, is called the principal quantum number. It is related to the number of nodes in the radial direction by an expression of the form $n - l - 1$ and specifies the different electron 'shells' of the atom, which are designated either by letters K, L, M, ..., Q, or by numbers 1, 2, 3, ..., 7, the largest number being seven. The second integer, l, is associated with the azimuthal angle θ and gives the number of antinodes between the two poles of Fig. 4.11. It is referred to as the azimuthal or orbital angular momentum quantum number for reasons which will be explained shortly and, by (4.74), it can assume the values 0, 1, 2, ..., $(n-1)$. In a hydrogen atom it has a second order effect on the value of the energy levels E_n which is due to an l-dependent relativistic correction to the mass of the electron. Now,

THE STATIONARY STATE

instead of a single energy level E_n associated with a given principal quantum number n we have several such levels, each corresponding to a different value of l—a situation which leads to the so-called *fine* structure
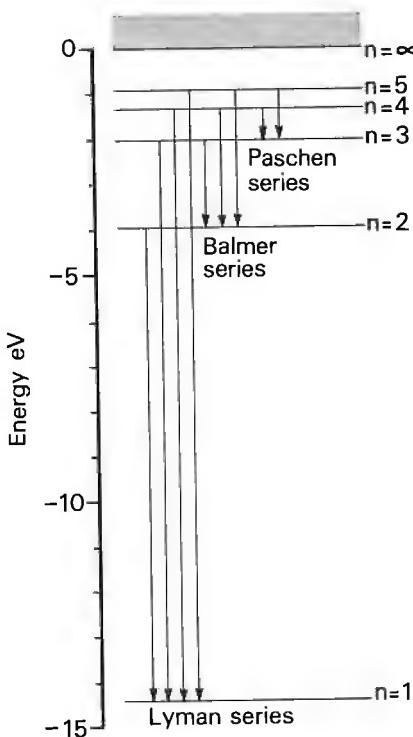

Fig. 4.16. Electron transitions between different energy levels in a hydrogen atom; Lyman, Balmer, and Paschen series.

of hydrogen lines.[13] From spectroscopy consecutive values of l are again referred to by letters (Paschen notation), as shown in Fig. 4.17, where, however, the corresponding differences in E_n are too small to be shown; the letters are s (sharp), p (principal), d (diffuse), f (fundamental), g, h, and i, the names recalling historical developments in spectroscopy. The numerical magnitude of energy corresponding to a given E_{nl} is called in spectroscopy a term value or simply a 'term'.[14] Finally, the third integer, m or m_l, is associated with the number of antinodes in the polar direction; it is called the magnetic quantum number for reasons to be explained later and, by (4.68), its magnitude $|m|$ is always less than or equal to l, its values extending over the interval $-l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l$.

In quantum mechanics, there is one more constant which is not necessarily an integer and which specifies an additional property of such

particles as an electron. This constant is called the spin quantum number and is usually designated by s. The physical reason for the existence of this number is the experimental fact that when, for example, an electron interacts with an electromagnetic field it behaves as if it had a small magnetic moment. An electric charge spinning on its own axis as it moves around the nucleus would have such a moment, but a strictly classical model is not really appropriate in this case, the physical situation being much more complex, since it involves the theory of relativity, as will be shown in chapter 9. However, assuming that the spin exists, we can now discuss its contribution to the energy levels E_{nl}. Since the electron has a charge and exhibits two kinds of angular momentum, orbital and spin,
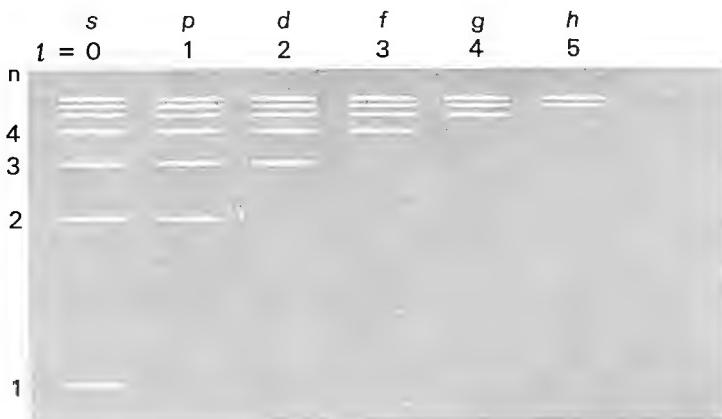
Fig. 4.17. Term diagram for the hydrogen atom.

each of them must give rise to a corresponding magnetic field. This leads to interaction which produces slight changes in the energy levels depending on the relative values of l and s, the so-called spin-orbit coupling, and constitutes an additional contribution to the fine structure of the line. However, the nucleus of an atom also has a spin and it generates its own magnetic field, which, in turn, interacts, very weakly, with the field generated by the electron. This interaction again affects the energy levels, giving rise to what is called the *hyperfine* structure of the line. This effect is approximately three orders of magnitude down on the previous effect, the magnetic moment being inversely proportional to the mass of the particle. Finally, it should be noted that the situation becomes much more complicated when an atom contains more than one electron. However, even then it is often possible to combine the orbital momentum l and the spin momentum s of individual electrons and to construct a joint orbital momentum L and a joint spin momentum S for the whole atom, capital letters now being used as a rule. A proper description of the

energy eigenstates of such systems, however, rapidly increases in complexity and will not be treated here, a clear and concise explanation being available elsewhere.[15]

4.7. Potential barriers

To broaden our investigations of the stationary state let us briefly consider the problem of potential barriers. So far we have assumed that the particle is bound, its energy being less than that required to leave a potential well of certain shape and depth; then the boundary conditions allow the existence of only those solutions which correspond to well-defined values of the total energy of the particle E. In the case of potential barriers (or troughs) the situation is reversed: the particle is free, so that its energy must be known in advance on arrival and cannot depend on the geometrical properties of the obstacle. This necessarily leads to a continuous rather than a discrete energy spectrum, since we can have any initial energy of the particle we choose. The three-dimensional case is of particular interest since it describes a collision.

Let us now consider, for simplicity, a one-dimensional system characterized by a potential barrier, as shown in Fig. 4.18, where $V(z) = V_0$ for $0 \leqslant z \leqslant a_z$ and $V(z) = 0$ everywhere else. If we assume that the particle
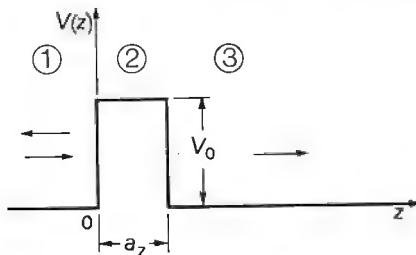
Fig. 4.18. One-dimensional potential barrier of height V_0 and width a_z.

approaches the barrier from the left, then for all $z < 0$ we have both the incident and reflected waves, whereas for $z > a_z$ we have only the transmitted wave. Again, this situation is strongly reminiscent of current and voltage reflections at discontinuities of an electrical transmission line, even to the extent that, as we shall see, the results are readily discussed both in quantum mechanics and in electrical engineering in terms of the reflection and transmission coefficients. Although we have already said that the initial energy of the particle can have any value we choose, in practice we can only have a laboratory or a 'box' of finite dimensions at our disposal, so that, in fact, the energy will still be quantized but the corresponding energy levels will be so close together that the steps between them can be assumed to be negligible; however, the finite size of the box makes the normalization of the corresponding wave functions

possible. This approach is particularly helpful if we combine it here with the so-called *periodic* boundary conditions, i.e., the boundary conditions which do not require zero value of the function Ψ at both ends of the interval, but merely the equality of its magnitude and slope, so that the actual shape of the wave function remains virtually unaffected by the introduction of the 'box'. Since the system is still assumed to be time-independent in the sense that we are only interested in the final result of a large number of identical experiments, we can separate the wave function Ψ into its time-dependent part $\psi_t(t)$ and time-independent part $\psi(z)$, as given by (4.13) and (4.16). The wave equation which has to be satisfied by ψ for all z outside the barrier is given by the one-dimensional equivalent of (4.18), viz.,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} = E\psi \tag{4.86}$$

This equation can be readily solved giving

$$\psi(z) = A_1\,e^{jkz} + B_1\,e^{-jkz}, \quad z \leqslant 0 \tag{4.87}$$

$$\psi(z) = A_3\,e^{jkz} \qquad\qquad z > a_z \tag{4.88}$$

where

$$k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} = \frac{p}{\hbar} \tag{4.89}$$

We can now see, multiplying both sides of (4.87) and (4.88) by $\psi_t(t) = \exp(-jEt/\hbar) = \exp(-j\omega t)$ that A_1 and A_3 are the respective amplitudes of the matter waves travelling to the right and B_1 is the amplitude of the matter wave travelling in the opposite direction. Also, our periodic boundary conditions made it possible for us to associate with a free particle a degenerate wave packet, consisting of a single component wave only, so that the corresponding $A(\beta)$ is now a δ-function (see (3.19)); this naturally makes the algebra of the problem much simpler.

Using a one-dimensional equivalent of (4.17) in the interval $0 \leqslant z \leqslant a_z$, putting $V = V_0$ and assuming that the energy of the particle $E > V_0$, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + (V_0 - E)\psi = 0 \tag{4.90}$$

Since $V_0 - E < 0$, the solution of (4.90) is given by

$$\psi(z) = A_2\,e^{jk_2z} + B_2\,e^{-jk_2z} \tag{4.91}$$

where

$$k_2 = \left(\frac{2m(E - V_0)}{\hbar^2}\right)^{\frac{1}{2}} \tag{4.92}$$

Since both ψ and $d\psi/dz$ must be continuous at $z=0$ and $z=a_z$, we now have four boundary conditions which must be satisfied. The equality of amplitude and slope at $z=0$ gives

$$2k_2 A_2 = (k+k_2)A_1 - (k-k_2)B_1 \tag{4.93}$$

$$2k_2 B_2 = -(k-k_2)A_1 + (k+k_2)B_1 \tag{4.94}$$

Also, substituting (4.93) and (4.94) in the two equations giving the equality of amplitude and slope at $z=a_z$, we obtain two ratios

$$\frac{B_1}{A_1} = \frac{1}{D}(k^2 - k_2^2)(1 - e^{2jk_2 a_z}) \tag{4.95}$$

$$\frac{A_3}{A_1} = \frac{1}{D} 4kk_2\, e^{j(k_2-k)a_z} \tag{4.96}$$

where

$$D = (k+k_2)^2 - (k-k_2)^2\, e^{2jk_2 a_z} \tag{4.97}$$

Equations (4.95) and (4.96) respectively express the amplitudes of the reflected and transmitted waves in terms of A_1, i.e., the amplitude of the incident wave. In practice, it is more convenient to use the reflection coefficient $R=|B_1/A_1|^2$ and the transmission coefficient $T=|A_3/A_1|^2$, where $R+T=1$. Calculating the square of the amplitude of (4.95) and (4.96) and substituting from (4.89) and (4.92) we obtain

$$\frac{1}{R} = 1 + \frac{4k^2 k_2^2}{(k^2 - k_2^2)\sin^2 k_2 a_z} = 1 + \frac{4E(E-V_0)}{V_0^2 \sin^2 k_2 a_z} \tag{4.98}$$

$$\frac{1}{T} = 1 + \frac{(k^2 - k_2^2)\sin^2 k_2 a_z}{4k^2 k_2^2} = 1 + \frac{V_0^2 \sin^2 k_2 a_z}{4E(E-V_0)} \tag{4.99}$$

The transmission coefficient is shown in Fig. 4.19 where T is plotted
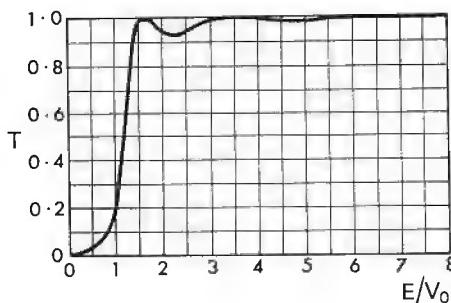
Fig. 4.19. Transmission coefficient for the potential barrier shown in Fig. 4.18. (From L. I. Schiff, *Quantum Mechanics*, 2nd ed., McGraw-Hill Book Company, New York, 1955.)

against E/V_0 for $mV_0a_z^2/\hbar^2 = 8$. It should be noted that for $E = V_0$ we obtain, since $\sin x/x \to 1$ as $x \to 0$,

$$\frac{1}{T} = 1 + \frac{mV_0a_z^2}{2\hbar^2} \tag{4.100}$$

For larger values of E the transmission coefficient oscillates in a manner which is well-known to electrical engineers. In particular, for $\sin k_2 a_z = 0$, that is, for $k_2 a_z = \{2m(E-V_0)/\hbar^2\}^{\frac{1}{2}} a_z = n\pi$ we obtain perfect transmission; now we have an integral number of half-wavelengths across the barrier (a resonance) so that the barrier is no longer 'seen' by the wave.

For energies $E < V_0$ the particle in classical mechanics could never surmount the barrier. Due to 'tunnelling' this is no longer so in quantum mechanics and we have a finite, although rapidly diminishing probability of the particle getting through the barrier even for $E < V_0$. Now the term $V_0 - E$ in (4.90) becomes positive so that in place of (4.91) we obtain the following solution

$$\psi(z) = A_2 \, e^{\alpha_2 z} + B_2 \, e^{-\alpha_2 z} \tag{4.101}$$

where

$$\alpha_2 = \left(\frac{2m(V_0 - E)}{\hbar^2} \right)^{\frac{1}{2}} \tag{4.102}$$

Introducing the boundary conditions and repeating the necessary calculations similar to (4.93)–(4.96) we find that the reflection and transmission coefficients are still the same, except for $\sinh \alpha_2 a_z$ in place of $\sin k_2 a_z$. Thus for $E < V_0$

$$\frac{1}{R} = 1 + \frac{4E(E-V_0)}{V_0^2 \sinh^2 \alpha_2 a_z} \tag{4.103}$$

$$\frac{1}{T} = 1 + \frac{V_0^2 \sinh^2 \alpha_2 a_z}{4E(E-V_0)} \tag{4.104}$$

Now the transmission coefficient rapidly approaches zero as $E \to 0$ and for $\alpha_2 a_z \gg 1$ we obtain, since $\sinh x \sim \frac{1}{2} e^x$ as $x \to \infty$

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\alpha_2 a_z} \tag{4.105}$$

There are several comments which can usefully be made at this point. First of all, the potential barrier giving rise to Fig. 4.19 is fairly 'opaque', the high value of eight for the important parameter $mV_0a_z^2/\hbar^2$ causing a relatively small departure from the classical step function for T. For an electron of mass $m = 9 \cdot 11 \times 10^{-31}$ kg we have $V_0a_z^2 = 0 \cdot 967 \times 10^{-37}$ J m$^2 = 0 \cdot 604 \times 10^{-18}$ eV m^2, so that even if the barrier is as little as 0·6 eV high its thickness is of the order of 10^{-9} m $= 10$ Å, which

is a very thin barrier indeed. Increasing the mass of the particle does not increase tunnelling because then the particle behaves more and more according to the laws of classical mechanics in which the transmission coefficient is zero for $E < V_0$ and unity for $E > V_0$. Secondly, in place of a potential barrier we could have had a potential trough. This would still lead to reflections, (4.92), (4.98), and (4.99) being still valid, except that now one would have to substitute $-V_0$ for $+V_0$ everywhere. Again, there is a close analogy between this and an electric transmission line, where reflections occur whenever we have a discontinuity in the parameters of the line, irrespective of sign. For a very deep trough, $E/V_0 \ll 1$, the probability that the particle will be transmitted is very small, but not zero, a situation which again has no equivalent in classical mechanics.

Finally, we should add that the discussion of three-dimensional obstacles leads naturally to the theory of collisions, which is extensively treated elsewhere[16] and will not be pursued further here.

4.8. Angular momentum

Let us now consider the important role played in quantum mechanics by the angular momentum. The importance of this concept is largely due to the fact that many systems of interest possess rotational symmetry, the associated boundary conditions being most readily expressed in terms of polar coordinates. In connection with such systems, the angular momentum often appears either as a constant of motion in classical mechanics or as an eigenvalue in quantum mechanics.

The usual definition of the angular momentum $\mathbf{M}$ of a particle about a point at a distance $\mathbf{r}$ is given by

$$\mathbf{M} = \mathbf{r} \times \mathbf{p} \tag{4.106}$$

where $\mathbf{p}$ is the linear momentum of the particle, as shown in Fig. 4.20, the cross indicating a vector product. It can be readily appreciated that the concept of an angular momentum is meaningless unless we have at
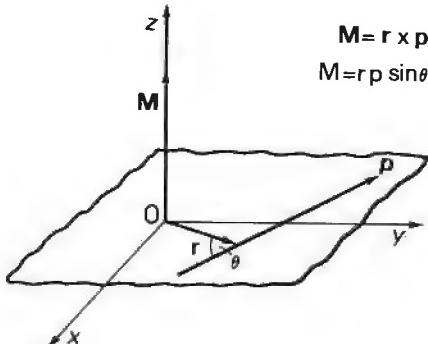

Fig. 4.20. The definition of angular momentum.

least two dimensions at our disposal. If all quantities in (4.106) are treated as operators, we obtain

$$\hat{\mathbf{M}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$$
$$= -j\hbar\hat{\mathbf{r}} \times \nabla \tag{4.107}$$

using the definition of the operator $\hat{\mathbf{p}}$, (3.55). With the help of (4.107) we can now write the following commutator

$$[\hat{M}_x, \hat{M}_y] = \hat{M}_x\hat{M}_y - \hat{M}_y\hat{M}_x$$
$$= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) - (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)$$
$$= \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] + \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z]$$
$$= j\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)$$
$$= j\hbar\hat{M}_z \tag{4.108a}$$

where (3.69) has been used. Similarly, we obtain for the remaining two components of the angular momentum operator (see problem 29)

$$[\hat{M}_y, \hat{M}_z] = j\hbar\hat{M}_x \tag{4.108b}$$

$$[\hat{M}_z, \hat{M}_x] = j\hbar\hat{M}_y \tag{4.108c}$$

the order in which the subscripts x, y, z are written being of importance. These equations show that no two components of the angular momentum commute, i.e., that there is a fundamental limit on the accuracy with which they can be measured simultaneously. However, we also find from (4.107) that they are all Hermitian, since both $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ have this property. Lastly, by forming commutators of the type $[\hat{M}^2, \hat{M}_x]$ we discover that these are all zero (see problem 30), so that the corresponding quantities commute and thus can be measured simultaneously with any desired degree of accuracy.

If the eigenfunctions of a system are expressed in terms of spherical polar coordinates, then, writing (x, y, z) as functions of (r, θ, ϕ) we obtain (see problem 28)

$$\hat{M}_x = j\hbar\left(\cot \theta \cos \phi \frac{\partial}{\partial \phi} + \sin \phi \frac{\partial}{\partial \theta}\right) \tag{4.109a}$$

$$\hat{M}_y = j\hbar\left(\cot \theta \sin \phi \frac{\partial}{\partial \phi} - \cos \phi \frac{\partial}{\partial \theta}\right) \tag{4.109b}$$

$$\hat{M}_z = -j\hbar \frac{\partial}{\partial \phi} \tag{4.109c}$$

where

$$\hat{M}^2 = -\hbar^2\left\{\frac{1}{\sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right\} \tag{4.110}$$

Let us now investigate the concept of angular momentum as it appears in connection with the hydrogen atom. By introducing a new function $\psi_r = rR(r)$ we can rewrite (4.70) in the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi_r}{\partial r^2} + \left\{V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right\}\psi_r = E\psi_r \tag{4.111}$$

This is the same as the one-dimensional equivalent of (4.17), provided we introduce a new potential function

$$\begin{aligned} V'(r) &= V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \\ &= -\frac{e^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \\ &= Ry\left\{-\frac{2}{(r/a_0)} + \frac{l(l+1)}{(r/a_0)^2}\right\} \end{aligned} \tag{4.112}$$

Thus, if the electron has a quantum number $l \neq 0$, then, in addition to the Coulomb force represented by $V(r)$, it experiences an additional force represented by the second term on the right-hand side of (4.112). If we were considering a classical particle of mass m, moving with angular velocity ω along the circumference of a circle of radius r, then its angular momentum would be given by

$$M = m\omega r^2 \tag{4.113}$$

Then, in order to keep the particle bound, an inward force of magnitude

$$m\omega^2 r = \frac{M^2}{mr^3} \tag{4.114}$$

would be required to balance the centrifugal force due to motion of the particle along an orbit. This additional force would have to be supplied by $V(r)$, thus lowering the additional energy required by the particle to free itself from the influence of the nucleus. Comparing the potential function $M^2/2mr^2$ corresponding to the force (4.114) and the second term in brackets in the first line of (4.112) one would suspect that

$$M = \{l(l+1)\}^{\frac{1}{2}}\hbar \tag{4.115}$$

As we shall see shortly, this relationship is in fact exactly true and, therefore, it is not surprising that the azimuthal quantum number l is often referred to as the orbital angular momentum quantum number.

The effective potential $V'(r)$ is plotted in Fig. 4.21 for three different values of l, the units for the two axes being respectively the Bohr atomic

radius a_0 and the Rydberg constant Ry. Figure 4.21 shows rather well the meaning of the restrictions imposed on l in (4.74); for example, when $n=0$. $E_n = -1Ry$, we can only have the bound state $l=0$. Similarly, for $n=1$, $E_n = -\frac{1}{4}Ry$ we can have $l=0$, 1 but not $l=2$ and so on, the effective role of $V(r)$ being gradually reduced as l increases. Finally, for positive values of E, the solutions of the wave equations (4.70) or (4.73) correspond to hyperbolic orbits in classical mechanics. Now the particle is no longer bound and the quantization of energy imposed by the boundary conditions is not required. Such solutions refer to free electrons and explain the existence of the continuous part of the spectrum.
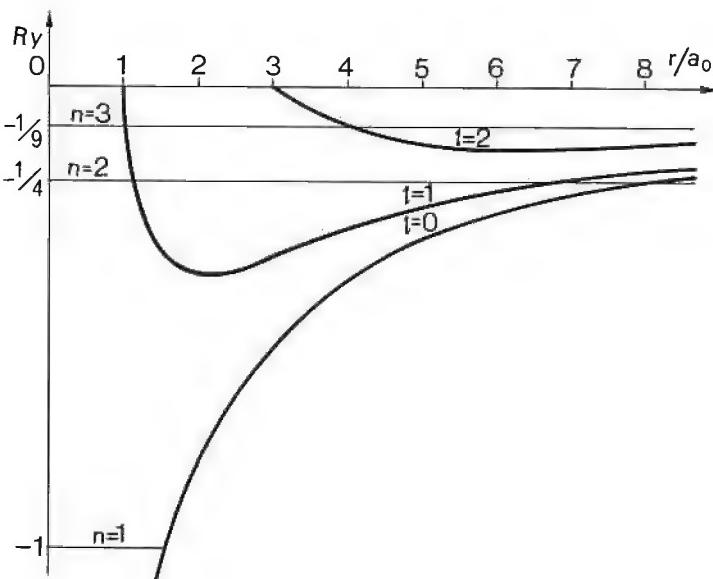
Fig. 4.21. The effective potential $V'(r)$ as a function of r, where r is measured in units of a_0 and the energy is measured in Rydbergs.

We can see from this discussion that, in quantum mechanics, a bound particle possesses angular momentum, according to (4.115), only when $l \neq 0$, i.e., when its wave function has lost spherical symmetry. This corresponds to a functional dependence of $\psi^*\psi$ on θ which, on the basis of Fig. 4.14, might possibly suggest something, at least vaguely resembling a particle orbit in classical mechanics. When $l=0$, the function $\psi^*\psi$ is perfectly symmetrical around the origin and no sign of a classical particle orbit is discernible.

Let us now calculate the expectation value of the magnitude of the angular momentum $\langle M^2 \rangle$. Substituting from (4.110) in (3.66) of chapter 3

and bearing in mind (4.65) and (4.67), we obtain

$$\langle \mathbf{M}^2 \rangle = \int \Psi^*_{nlm} \hat{\mathbf{M}}^2 \Psi_{nlm} \, d\tau$$

$$= -\hbar^2 \int \Psi^*_{nlm} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \Psi_{nlm} \, d\tau$$

$$= \hbar^2 \int \Psi^*_{nlm} l(l+1) \Psi_{nlm} \, d\tau$$

$$= \hbar^2 l(l+1) \qquad (4.116)$$

which confirms our inspired guess, (4.115). Further calculations show that the standard deviation is zero (see problem 32) and $M^2 = \hbar^2 l(l+1)$, the particle being in an eigenstate. Also we find, comparing (4.67), (4.110), and (3.65), that (4.67) is the eigenvalue equation associated with the operator $\hat{\mathbf{M}}^2$, $l(l+1)\hbar^2$ are its eigenvalues and $\Theta_{lm}(\theta)$ the corresponding eigenfunctions.

Let us now consider the z component of the angular momentum M_z. Its mean value $\langle M_z \rangle$ for a hydrogen atom can now be calculated by substituting the third of (4.109c) in (3.66). We then obtain, in view of (4.76),

$$\langle M_z \rangle = \int \Psi^*_{nlm} \hat{M}_z \Psi_{nlm} \, d\tau$$

$$= -j\hbar \int \Psi^*_{nlm} \frac{\partial}{\partial \phi} \Psi_{nlm} \, d\tau$$

$$= m\hbar \int \Psi^*_{nlm} \Psi_{nlm} \, d\tau$$

$$= m\hbar \qquad (4.117)$$

Since the standard deviation in this case is again equal to zero (see problem 33), $M_z = m\hbar$ and the system again is in an eigenstate. A comparison of (4.65), (4.109c), and (3.65) now reveals that (4.65) is the eigenvalue equation for M_z, $m\hbar$ its eigenvalues and $\Phi_m(\phi)$ the respective eigenfunctions. However, we can talk about $\hat{M}_z$ or $\langle M_z \rangle$ only when the direction of the z-axis is defined, e.g., by relating it to some other direction, such as that of an external magnetic field. For this reason m (or m_l, to distinguish it from m_s which is related to the spin quantum number s) is usually referred to as the magnetic quantum number.

From (4.116) and (4.117) the quantization expressed by m_l does not affect the magnitude of the angular momentum $\mathbf{M}^2$. It is therefore convenient to treat $\langle \mathbf{M}^2 \rangle$ as the mean square of the length of a vector $\mathbf{M}$, except that the length of the vector is given by $\{l(l+1)\}^{\frac{1}{2}}\hbar$ rather than $l\hbar$,

which would be more usual. Since the quantization expressed by m_l does not affect the length of **M**, it must be a 'spatial' quantization, the vector **M** being allowed to adopt only certain positions with respect to an external direction. It is convenient to represent all possible values of $\langle M_z \rangle$ as projections of a vector of length $\{l(l+1)\}^{\frac{1}{2}}\hbar$ on the z-axis, as shown in Fig. 4.22, where $l=1$. (This representation is rather arbitrary, some authors still choosing a vector of length $l\hbar$, so that, for example, in Fig. 4.22, we would have simply three arrows, up, down, and horizontal.
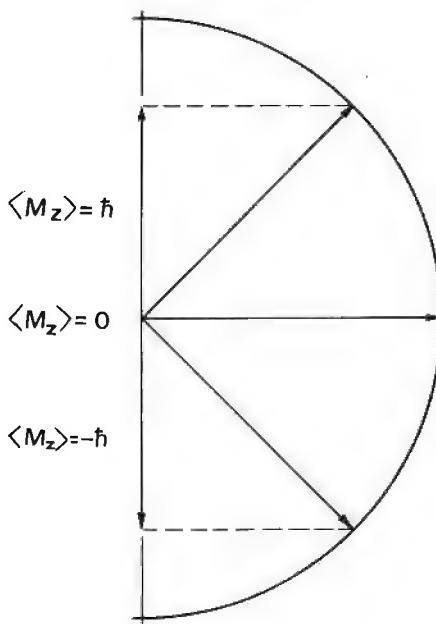
Fig. 4.22. Vector representation of the angular momentum eigenvalues.

However, this convention is based on the 'old' quantum mechanics and should not be encouraged.) The convenience of this representation resides in the fact that it facilitates the calculation of the joint effect of spin and orbital momentum by introducing the laws of vector algebra.[17] Also, the usual restriction on the values of m_l, which, according to (4.74), only extend from $-l$ to $+l$, is now automatically satisfied, there being only $2l+1$ possible values of m_l.

We can now see that the orbital angular momentum of a particle can be quantized both in magnitude and direction. The magnitude quantization finds its confirmation in corrections to the energy eigenvalues E_n corresponding to the same n but different l, as was discussed in connection with Fig. 4.17. The additional quantization of the M_z component or the spatial quantization of **M**, can only be observed when there are

means for relating the z-axis of the system, e.g., an atom, to some fixed direction in space. As has been already pointed out, this can be done most readily by introducing an external magnetic field. Since an electron carries electric charge, its movement in space gives rise to a magnetic dipole similar to that generated by an equivalent current loop, provided the electron is in a quantum state $l \neq 0$. In classical terms, the strength of such a magnetic dipole is given by the usual expression of current times the loop area. Using this approach we obtain from (4.113) and (4.115)

$$\mu_l = -\frac{e\omega}{2\pi}\pi r^2$$

$$= -\tfrac{1}{2}e\omega r^2$$

$$= -\frac{eM}{2m}$$

$$= -\frac{e\hbar}{2m}\{l(l+1)\}^{\frac{1}{2}} \tag{4.118}$$

where $e\hbar/2m = 9.27 \times 10^{-24}$ amp m^2 is the so-called Bohr magneton. Since the energy of an atom in state l and subject to the action of a magnetic field $\mathbf{B}$ directed along the z-axis depends on the product $\mu_z B = m_l \mu_l B$, where $\mu_z = m_l \mu_l$, and since m_l can have $2l+1$ values only, this gives rise, neglecting spin, to $2l+1$ additional transitions or lines, as indicated in Fig. 4.23 for $l=1$. Thus, in a uniform magnetic field, the
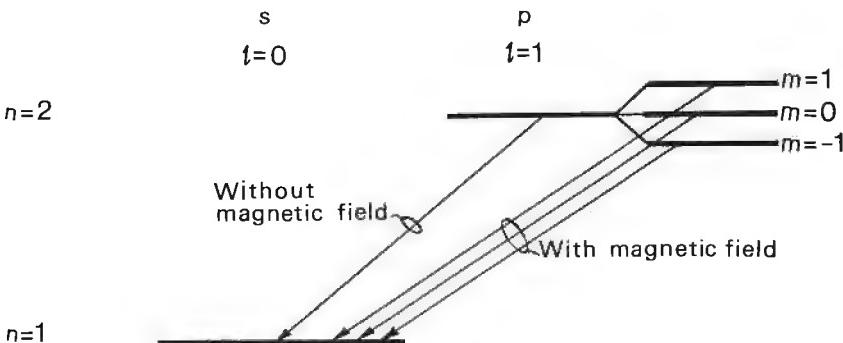
Fig. 4.23. Splitting of energy levels due to quantization of M_z—the Zeeman effect. (The additional doubling of levels due to electron spin is not shown.)

individual energy levels which are now designated by E_{nl}, and bearing in mind the slight corrections due to different values of l, further split into m_l sublevels, giving rise in the corresponding line spectra to the so-called *Zeeman effect*.

The quantization of M_z is displayed even more convincingly in the

celebrated Stern and Gerlach experiment,[18] shown schematically in Fig. 4.24 although, in this case, the angular momentum is spin, not orbital. Here, use is made of the fact that when a magnetic dipole is immersed in a non-uniform magnetic field it experiences a translation force, the two 'end charges' of the magnetic dipole 'seeing' a different value of **B**. In fact, the force is simply given by

$$F = \mu_z \frac{\partial \mathbf{B}_z}{\partial z} \tag{4.119}$$

if the field is assumed to change in the z-direction only. Since, in our case, $\mu_z = m_l \mu_l$, atoms in different m_l states will experience different forces. Stern and Gerlach put this argument to test by sending a fine beam of silver atoms along suitably shaped pole pieces of a very strong magnet, as shown
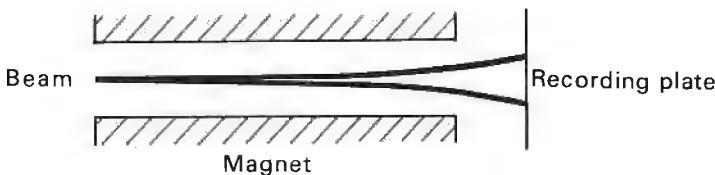
Fig. 4.24. The Stern–Gerlach experiment.

in Fig. 4.24. Although the atoms exhibited no orbital angular momentum ($L=0$) the presence of the resultant spin angular momentum associated with $S=\frac{1}{2}$ led to two separate quantum states, $M_S = -\frac{1}{2}, \frac{1}{2}$. (As previously stated, it is customary to use capital letters for the resultant quantum numbers of an atom comprising several electrons.) When the beam was sent through the magnetic field, depending on the value of M_S, the atoms were deflected either upwards or downwards, giving rise to two separate spots on the recording plate. If the spatial quantization had not occurred, the atoms could have had all possible directions in space and a continuous vertical line would have appeared on the recording plate in place of two separate spots.

Problems

1. Show how to derive the E_x and E_y or H_x and H_y components of the electromagnetic field, once the corresponding E_z and H_z components are known. Are there any limitations to this procedure?

2. State briefly why the possibility of expanding an arbitrary periodic function in terms of a Fourier series helps to simplify the solution of (4.1).

3. Substitute (4.5) in (4.2) and show that (4.2) reduces to a set of ordinary differential equations (4.6). Solve (4.6) to obtain (4.8) and then substitute the boundary conditions (4.4). You should now obtain (4.9).

4. Discuss the way in which the boundary conditions (4.4) limit the number of possible solutions of (4.2). What is the physical explanation of the fact that only integral values of l, m, n satisfy the boundary conditions, and thus (4.2)?

5. Discuss the relationship between (4.14) and the general eigenvalue equation for operators, (3.65). Why is (3.65) called the eigenvalue equation?

6. Using the definition of $\hat{H}$, show that (4.17) can be expressed in the form $\hat{H}\psi = E\psi$. Is there any similarity between this equation and (4.14), when the latter is multiplied by ψ? Remember that $H = E$ only for conservative systems.

7. Discuss the time-independent Schrödinger equation for $\Psi^*(\mathbf{r}, t)$ starting with (3.23) of chapter 3 and separating the variables. Does this agree with the definition of Ψ^*?

8. Can you guess, by comparing (4.2) and (4.18), why a bound particle can only possess certain well defined values of energy E? (Remember $E = h\nu = \hbar\omega$.) This point is discussed more fully in section 4.3.

9. Discuss the physical significance of discontinuities and infinite values of Ψ and $\nabla\Psi$. Use the concept of probability density function $\Psi^*\Psi$ and (3.55).

10. Integrate (4.22) and derive the correct value for the normalization constant.

11. Calculate the mean energy, position, and linear momentum of a particle in an infinitely deep, one-dimensional potential well. Can you obtain the corresponding wave function straight from (4.22)? What is the value of the normalization constant now? Draw the new probability density function $\Psi^*\Psi$ for the first few energy states. How is it related to (4.26) and Fig. 4.2?

12. Bearing in mind problem 11, derive and plot A^*A for the case of a one-dimensional potential well of infinite depth. Calculate $\langle p \rangle$ and σ_p using A^*A instead of $\Psi^*\Psi$.

13. Repeat problem 12 for a three-dimensional potential well of infinite depth.

14. Show that from (3.55) and (3.65) of chapter 3 we obtain the following eigenvalue equation for the momentum operator

$$(\hbar/j)\nabla A(\mathbf{k}) = \mathbf{p}A(\mathbf{k})$$

Since $A(\mathbf{k})$ does not depend on time, show that $A(\mathbf{k}) = \exp(j\mathbf{p}\cdot\mathbf{r}/\hbar) = \exp(j\mathbf{k}\cdot\mathbf{r})$ is an eigenfunction solution of this equation.

15. Write down expressions for current or voltage along a loss-less and a purely resistive transmission line. Compare these to (4.18) and (4.30).

16. Calculate the wave function for a particle bound in the double

potential well shown in Fig. 4.7, where $E < V_1$, $b_z \ll a_z$. Assume that the particle is initially in the first well. Discuss the physical meaning of the shape of $\Psi^*\Psi$. How does this differ from the results obtained using the laws of classical mechanics?

17. Calculate the wave equation for a particle contained in the potential well shown below. Sketch the corresponding probability density function $\Psi^*\Psi$. Assume that the particle is in a state $E_n > V_1$. What would have happened if we had assumed $E_n < V_1$?
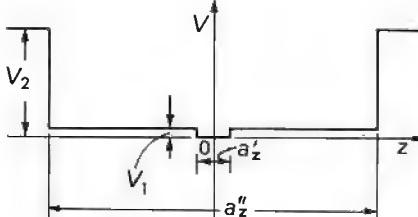
18. Consider a simple harmonic oscillator. Calculate, using the laws of classical mechanics, the probability density function for a particle to be found at a point ζ, assuming that the amplitude of oscillation is given by ζ_0. Show that your expression is the same as (4.48). (Remember that harmonic motion is the projection on the diameter of a circle of the motion with constant ω along its circumference.)

19. Discuss the differences between thermal and quantum noise. What happens at absolute zero, $T = 0°\text{K}$?

20. Calculate $\langle p \rangle$, $\langle p^2 \rangle$, and σ_p for a harmonic oscillator in the ground state $(n=0)$ using the probability density function A^*A of (4.62).

21. Calculate $\langle E \rangle$, σ_E, and $\sigma_z \sigma_p$ for a harmonic oscillator when $n=1$.

22. Derive an expression for the Laplacian in polar spherical coordinates and show that Schrödinger's time-independent wave equation is given by (4.63).

23. Discuss the use of m for $|m|$ in (4.68). What would happen if we allowed m to be negative here?

24. Show from (4.67) that Θ_{lm} is well behaved near the origin for $m = \pm 1$ if $\Theta = k\theta$ for small θ.

25. Write (4.67) in finite difference form and show that $m \leq l$ must be satisfied in order to avoid a pole at $\theta = n\pi$. Start with $\Theta = 0$ or $d\Theta/d\theta = 0$ at 90° and consider the sign of the curvature.

26. Why is $E < 0$ for an electron bound to a positive nucleus? What would happen if E were greater than zero?

27. Using (4.76) write the eigenfunctions of a hydrogen atom for the energy state $n = 3$.

28. Explain why at least two dimensions are required for the concept of angular momentum.

29. Calculate $[\hat{M}_y, \hat{M}_z]$ and $[\hat{M}_z, \hat{M}_x]$ using (4.108a) and show that (4.108b) and (4.108c) are correct. What would happen if we reversed the order of terms in any one of these expressions?

30. Show that $[\hat{M}^2, \hat{M}_x]$, $[\hat{M}^2, \hat{M}_y]$, and $[\hat{M}^2, \hat{M}_z]$ are all zero. (Use the expressions obtained in problem 19 of chapter 3.)

31. Express the operators $\hat{M}_x$, $\hat{M}_y$, and $\hat{M}_z$ in terms of spherical polar coordinates and show that (4.109) and (4.110) are correct.

32. Calculate $\langle M^4 \rangle$ for a hydrogen atom and show that the standard deviation $\langle M^4 \rangle - \langle M^2 \rangle^2 = 0$. (See (4.116).)

33. Show that the standard deviation $\langle M_z^2 \rangle - \langle M_z \rangle^2 = 0$ for a hydrogen atom, where $\langle M_z \rangle$ is given by (4.117).

34. Show, using the ordinary laws of magnetostatics, that (4.119) gives the z-directed component of force on a magnetic dipole of moment $\boldsymbol{\mu}$ immersed in a non-homogeneous magnetic field **B**.

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5. Degeneracy, Orthogonality, and Composite States

The fact that several modes of a resonant circuit or cavity may have the same resonant frequency is familiar to electrical engineers; the same applies to the observation that a resonant system may support more than a single mode at the same time. Both these phenomena, although they have a simple origin, acquire added physical significance in quantum mechanics and should therefore be discussed in some detail.

5.1. Degeneracy

We have already considered in chapter 4 the general problem of a bound particle, both in one and three dimensions. In the one-dimensional case which, by its very nature, is only hypothetical in character, the determination of the energy eigenvalues E_n is quite unambiguous, as can be seen, for example, in Figs. 4.5a, b. To each value of n corresponds a different value of E, the eigenvalues E_n forming a singly infinite series. However, in the case of a three-dimensional system, the situation is more complicated, as can be seen from (4.10) or (4.23). Here the resonances ω_{lmn}, in the case of a resonant cavity, or the energy eigenvalues E_{lmn}, in the case of a bound particle, form a triply infinite series, to each triplet of integers l, m, n corresponding a value of ω or E. The question now arises; are these values always different, or is it possible to have the same values of ω or E for, let us say, two different combinations of l, m, n?

We can answer this question quite easily by inspecting (4.23), which gives the energy eigenvalues for a particle confined inside an infinitely deep, rectangular potential well. Let us assume that $a_x = a_y = a_z$, so that our potential box becomes a cube of side a_x. It can then be seen from (4.23) that the same value of E corresponds, for example, to the following combinations of the integers l, m, n,

l	m	n
2	1	1
1	2	1
1	1	2

or

$$\begin{matrix} 2 & 2 & 1 \\ 2 & 1 & 2 \\ 1 & 2 & 2 \end{matrix}$$

and so on. Thus, to each value of E now correspond several different combinations of l, m, n, each combination specifying a different wave function ψ. This clearly suggests that the geometrical symmetry of the system is closely related to the concept of degeneracy, since it allows different wave patterns corresponding to different combinations of l, m, n, to be obtained by a mere rotation of the whole system. Furthermore, the order of degeneracy seems to be closely related to the degree of symmetry of the system, the greater the symmetry, the higher the order of degeneracy. It should be added that the word 'symmetry' is used here in a very broad sense. For example, in a rectangular box, the degeneracy may occur even when the three sides a_x, a_y, a_z are all different, but stand in a simple ratio, for example, $a_x = 2a_y$. Then from (4.23) of chapter 4, the following values of l, m, n, for example, give the same value of E and lead to degeneracy

l	m	n
4	1	1
2	2	1

or

$$\begin{matrix} 8 & 2 & 1 \\ 4 & 4 & 1 \end{matrix}$$

and so on.

It is not unreasonable to expect that, in view of the inherent symmetry of the systems encountered in nature, especially on the atomic scale, degeneracy is more a rule than an exception. In many cases, the degeneracy complicates various calculations, as we shall see in chapter 6, where the perturbation method of calculating the eigenvalues and eigenstates of a system is discussed, but quite often the symmetry properties of very complicated systems are used to introduce some order into their analysis. A good example of the effect of symmetry is provided by the elementary treatment of the hydrogen atom, as shown in section 4.6 of chapter 4. Since, in this case, the electron is assumed to be subject to the force due to a three-dimensional hyperbolic well $V = -e^2/4\pi\varepsilon_0 r$ only and since this force is perfectly symmetrical, V being a function of the distance r between the two particles, the expression for the eigenvalues E_n given by

(4.78) is a function of n and does not contain the other two quantum numbers l and m. This extreme symmetry is destroyed, however, when we consider the relativity correction and the interaction between orbital and spin magnetic moments, which remove the l degeneracy, and the spatial quantization in the presence of a magnetic field which removes the m degeneracy (Zeeman splitting).

A more general insight into the problem of degeneracy can be obtained by the study of group theory, which deals with the more difficult and less immediately obvious symmetry properties; this approach is very powerful but also rather difficult.[1,2] However, it is indispensable for a meaningful discussion of some of the more involved systems of quantum mechanics, such as heavy atoms or molecules.

5.2. General properties of eigenfunctions

In section 3.3 we discussed the normalization of the wave functions Ψ and established a general condition (3.18) which was used in normalizing the wave functions of chapter 4. In doing this, we might have noticed that integrals of the form $\int \Psi_m^* \Psi_n \, d\mathbf{r}$ were invariably equal to zero, except when $m = n$. We are now going to discuss this point more fully.

Let us consider the time-independent Schrödinger equation, (4.17). In the case of two different solutions or eigenstates m and n, we have

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V(\mathbf{r})\psi_n = E_n \psi_n$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_m^* + V(\mathbf{r})\psi_m^* = E_m \psi_m^*$$

(5.1)

(In view of (4.16), both ψ and ψ^* satisfy the same differential equation. This does not apply to Ψ and Ψ^*, as is shown by (3.22) and (3.23).) Multiplying the first of (5.1) by ψ_m^* and the second by ψ_n, integrating and subtracting, we obtain

$$-\frac{\hbar^2}{2m} \int (\psi_m^* \nabla^2 \psi_n - \psi_n \nabla^2 \psi_m^*) \, d\mathbf{r} = (E_n - E_m) \int \psi_m^* \psi_n \, d\mathbf{r} \qquad (5.2)$$

In view of (3.74), the left-hand side of (5.2) is identically equal to zero, so that the right-hand side must also be zero at all times. But, for non-degenerate systems, $E_n \neq E_m$ by definition, unless $n = m$, so that the integral appearing on the right-hand side of (5.2) must be zero, except when $m = n$. This important property of energy eigenfunctions is called orthogonality. Since the wave functions are also normalized, they are then described as orthonormal. (The treatment of degenerate cases, when $E_n = E_m$ although $n \neq m$, will be discussed in chapter 6.)

Orthogonal functions have one very valuable property—they can be used for expanding more complicated functions which may be less

amenable to algebraic manipulation. The best example are trigonometric functions which are frequently used in the form of Fourier series for expanding arbitrary periodic functions. The same applies to the eigenfunctions ψ_n, provided that they form what is called a complete set, as trigonometric functions do. Broadly speaking, a complete set is a set which comprises a sufficient number of functions to represent with unlimited accuracy a class of arbitrary functions, and in this case requires that there should be no other function $u(\mathbf{r}) \neq \psi_n(\mathbf{r})$ satisfying the relationship $\int u(\mathbf{r})\psi_n(\mathbf{r})\, d\mathbf{r} = 0$. It is possible to show[3, 4, 5] that the energy eigenfunctions do form, in general, a complete set and thus can be used for expanding other wave functions encountered in quantum mechanics.*

5.3. Composite states

In chapter 4 we discussed the so-called 'stationary' or 'pure' states which are characterized by the fact that the particle is in a single energy state only. The wave function of the system is then represented by a single energy eigenfunction, say, Ψ_n. This is not the only way in which the bound particle may behave however. There is nothing to prevent the particle from being in a composite energy state, just as there is nothing to prevent a resonant cavity from simultaneously resonating in several modes, provided that we choose to excite them. Let us therefore investigate the consequences of such a situation in quantum mechanics.

The simplest case to consider is that in which the wavefunction of the system must be represented by a sum of two energy eigenfunctions Ψ_m and Ψ_n, namely

$$\Psi = a_m \Psi_m + a_n \Psi_n \tag{5.3}$$

where a_m and a_n are constants. What does (5.3) mean as far as the general properties of the particle are concerned? First of all let us investigate the probability density function of the system $\Psi^*\Psi$. Since from (5.3) the wavefunction of the system is now given by

$$\Psi = a_m \psi_m\, e^{-jE_m t/\hbar} + a_n \psi_n\, e^{-jE_n t/\hbar} \tag{5.4}$$

its complex conjugate is

$$\Psi^* = a_m^* \psi_m^*\, e^{jE_m t/\hbar} + a_n^* \psi_n^*\, e^{jE_n t/\hbar} \tag{5.5}$$

Now (5.4) must be a solution of Schrödinger's equation, (3.22), since the equation is linear and Ψ is a linear combination of two known solutions, Ψ_m and Ψ_n. By the same reasoning Ψ^* is a solution of the conjugate Schrödinger equation, (3.23). But the integral of $\Psi^*\Psi$ over the whole space must be equal to unity, i.e., Ψ must be normalized, since the particle is undoubtedly situated somewhere in the system. Substituting

---

* In general the eigenfunctions of any operator representing an observable form a complete set.

(5.4) and (5.5) in the usual expression for normalization, we obtain

$$
\int \Psi^*\Psi \, d\mathbf{r} = a_m^* a_m \int \Psi_m^* \Psi_m \, d\mathbf{r} + a_n^* a_n \int \Psi_n^* \Psi_n \, d\mathbf{r}
$$

$$
+ a_m^* a_n \int \Psi_m^* \Psi_n \, d\mathbf{r} + a_n^* a_m \int \Psi_n^* \Psi_m \, d\mathbf{r}
$$

$$
= a_m^* a_m + a_n^* a_n = 1 \tag{5.6}
$$

where we have used the orthogonal properties of the eigenfunctions Ψ_m and Ψ_n. Equation (5.6) imposes the following condition on the coefficients a: the squares of their magnitudes must add up to unity. Extending this reasoning to a larger number of terms we can show that, in general, when the wavefunction Ψ is a sum of n eigenfunctions Ψ_n,

$$
\sum_n a_n^* a_n = 1 \tag{5.7}
$$

(see problem 6).

Substituting from (5.4) and (5.5) we now find that the probability density function

$$
\Psi^*\Psi = (a_m^* \Psi_m^* + a_n^* \Psi_n^*)(a_m \Psi_m + a_n \Psi_n)
$$

$$
= a_m^* a_m \psi_m^* \psi_m + a_n^* a_n \psi_n^* \psi_n + a_m a_n^* \psi_m \psi_n^* \, e^{-j(E_m - E_n)t/\hbar}
$$

$$
+ a_m^* a_n \psi_m^* \psi_n \, e^{j(E_m - E_n)t/\hbar} \tag{5.8}
$$

Equation (5.8) clearly shows that the new probability density function is time-dependent. When, in chapter 4, the particle was assumed to be in a single energy state E_n, the corresponding probability density function $\Psi^*\Psi = \psi^*\psi$ was time-independent. Indeed, this is the very reason why such states are useful in describing time-independent systems, such as non-radiating atoms. Then, any observation of energy of such a system would give us a single value for E, as shown in Fig. 5.1. Also, although observation of position or momentum of the particle would have a spread, the corresponding probability distributions would still be time-independent. In the case of a system which is represented by a wavefunction of the type shown in (5.3), however, the energy of the system is no longer
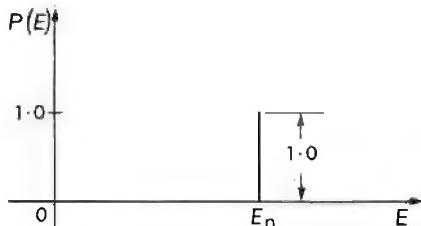
Fig. 5.1. Probability distribution of energy for a particle in an energy eigenstate n.

single-valued, although it is still time-independent (see Fig. 5.2) and the mean position of the particle becomes a function of time, as if the particle were actually moving from one end of the system to the other.
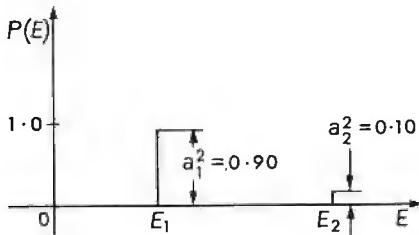
Fig. 5.2. Probability distribution of energy for a particle in a 'composite' state.

5.4. Composite states for a particle bound in an infinitely deep, one-dimensional potential well

The best way to see the differences between stationary and composite states is to consider a simple example, such as that provided by a particle bound in a one-dimensional, rectangular potential well of infinite depth. We know from (4.22) and (4.23) that, if the width of the well is a_z, the normalized wavefunctions of the system are given by

$$\Psi_n = \left(\frac{2}{a_z}\right)^{\frac{1}{2}} \sin \frac{n\pi z}{a_z} e^{-jE_nt/\hbar} \tag{5.9}$$

where

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma_z^2} \tag{5.10}$$

m being the mass of the particle. Let us first assume that the system is in its nth eigenstate. Then, making use of the energy operator $j\hbar(\partial/\partial t)$, we obtain

$$\langle E \rangle = \int \Psi_n^* \left(j\hbar \frac{\partial}{\partial t}\right) \Psi_n \, dz$$

$$\frac{2}{a_z} \int_0^{a_z} E_n \sin^2 \frac{n\pi z}{a_z} \, dz$$

$$= E_n \tag{5.11}$$

$$\langle E^2 \rangle = \int \Psi_n^* \left(-\hbar^2 \frac{\partial^2}{\partial t^2}\right) \Psi_n \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} E_n^2 \sin^2 \frac{n\pi z}{a_z} \, dz$$

$$= E_n^2 \tag{5.12}$$

$$\sigma_E^2 = \langle E_n^2 \rangle - \langle E_n \rangle^2 = 0 \tag{5.13}$$

Similarly, introducing the position and momentum operators $\hat{z}$ and $-j\hbar(\partial/\partial z)$, we obtain

$$\langle z \rangle = \int \Psi_n^* z \Psi_n \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} z \sin^2 \frac{n\pi z}{a_z} \, dz$$

$$= \tfrac{1}{2} a_z \qquad (5.14)$$

$$\langle z^2 \rangle = \int \Psi_n^* z^2 \Psi_n \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} z^2 \sin^2 \frac{n\pi z}{a_z} \, dz$$

$$= \frac{a_z^2}{3} - \frac{a_z^2}{2n^2\pi^2} \qquad (5.15)$$

$$\sigma_z^2 = \langle z^2 \rangle - \langle z \rangle^2 = \frac{a_z^2}{12} - \frac{a_z^2}{2n^2\pi^2} \qquad (5.16)$$

and

$$\langle p \rangle = \int \Psi_n^* \left(-j\hbar \frac{\partial}{\partial z} \right) \Psi_n \, dz$$

$$= -j\hbar \frac{2}{a_z} \int_0^{a_z} \frac{n\pi}{a_z} \sin \frac{n\pi z}{a_z} \cos \frac{n\pi z}{a_z} \, dz$$

$$= 0 \qquad (5.17)$$

$$\langle p^2 \rangle = \int \Psi_n^* \left(-\hbar^2 \frac{\partial^2}{\partial z^2} \right) \Psi_n \, dz$$

$$= \hbar^2 \frac{2}{a_z} \int_0^{a_z} \frac{n^2\pi^2}{a_z^2} \sin^2 \frac{n\pi z}{a_z} \, dz$$

$$= \frac{n^2\pi^2\hbar^2}{a_z^2} \qquad (5.18)$$

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \frac{n^2\pi^2\hbar^2}{a_z^2} \qquad (5.19)$$

These equations confirm what we have already stated, viz., if a system is in a stationary state, its energy is single-valued and its probability density function $\Psi^*\Psi$ is time-independent, as are $\langle z \rangle$, $\langle p \rangle$, σ_z, and σ_p. Furthermore, we find from (5.10) and (5.19) that, in this case,

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} \qquad (5.20)$$

which is reminiscent of a corresponding expression in classical mechanics for the kinetic energy of a particle. Finally, as $n \to \infty$

$$\sigma_z^2 \to \frac{a_z^2}{12} \tag{5.21}$$

which is also the variance of position for a classical particle moving with constant velocity in a flat-bottomed, one-dimensional well (see problem 7).

Let us now consider the same system as before, but assume that it is in a composite state, characterized by, let us say, the occupancy of the first two energy levels E_1 and E_2. The wavefunction of the system is now given by

$$\Psi = a_1 \Psi_1 + a_2 \Psi_2$$

$$= a_1 \left(\frac{2}{a_z}\right)^{\frac{1}{2}} \sin \frac{\pi z}{a_z} e^{-jE_1 t/\hbar} + a_2 \left(\frac{2}{a_z}\right)^{\frac{1}{2}} \sin \frac{2\pi z}{a_z} e^{-jE_2 t/\hbar} \tag{5.22}$$

where a_1 and a_2 are real and

$$a_1^2 + a_2^2 = 1 \tag{5.23}$$

The probability density function $\Psi^*\Psi$ must now be time-dependent due to the presence of cross-product 'interference' terms. Substituting from (5.22) we obtain

$$\Psi^*\Psi = a_1^2 \frac{2}{a_z} \sin^2 \frac{\pi z}{a_z} + a_2^2 \frac{2}{a_z} \sin^2 \frac{2\pi z}{a_z}$$

$$+ 2a_1 a_2 \frac{2}{a_z} \sin \frac{\pi z}{a_z} \sin \frac{2\pi z}{a_z} \cos \frac{E_1 - E_2}{\hbar} t \tag{5.24}$$

For convenience, Fig. 5.3 shows the three terms of (5.24) separately; Fig. 5.4 then gives the probability density function $\Psi^*\Psi$ for $a_1^2 = 0.90$ and $a_2^2 = 0.10$ and for four different values of t.

Let us now calculate both $\langle E \rangle$ and $\langle E^2 \rangle$ of the new system. Substituting from (5.22) we obtain

$$\langle E \rangle = \int \Psi^* \left(j\hbar \frac{\partial}{\partial t}\right) \Psi \, dz$$

$$= \int (a_1^* \Psi_1^* + a_2^* \Psi_2^*)(a_1 E_1 \Psi_1 + a_2 E_2 \Psi_2) \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} \left(a_1^2 E_1 \sin^2 \frac{\pi z}{a_z} + a_2^2 E_2 \sin^2 \frac{2\pi z}{a_z} \right.$$

$$\left. + 2a_1 a_2 E_1 E_2 \sin \frac{\pi z}{a_z} \sin \frac{2\pi z}{a_z} \cos \frac{E_1 - E_2}{\hbar} t \right) dz$$

$$= a_1^2 E_1 + a_2^2 E_2 \tag{5.25}$$

and

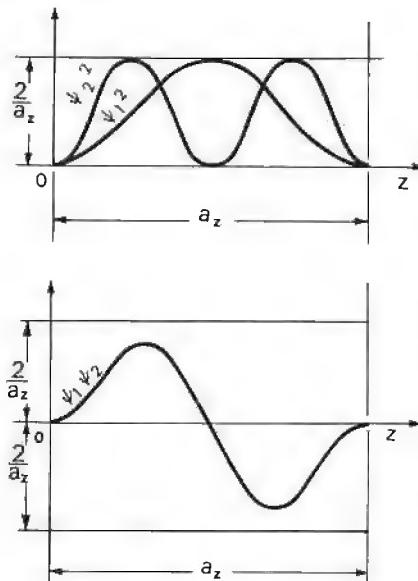$$\langle E^2 \rangle = \int \Psi^* \left(-\hbar^2 \frac{\partial^2}{\partial t^2} \right) \Psi \, dz$$

$$= \int (a_1^* \Psi_1^* + a_2^* \Psi_2^*)(a_1 E_1^2 \Psi_1 + a_2 E_2^2 \Psi_2) \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} \left(a_1^2 E_1^2 \sin^2 \frac{\pi z}{a_z} + a_2^2 E_2^2 \sin^2 \frac{2\pi z}{a_z} \right.$$

$$\left. + 2a_1 a_2 E_1^2 E_2^2 \sin \frac{\pi z}{a_z} \sin \frac{2\pi z}{a_z} \cos \frac{E_1 - E_2}{\hbar} t \right) dz$$

$$= a_1^2 E_1^2 + a_2^2 E_2^2 \qquad (5.26)$$

Fig. 5.3. The three functions ψ_1^2, ψ_2^2, and $\psi_1 \psi_2$ for a particle confined in an infinitely deep one-dimensional potential well.

We now find that the variance of the energy distribution function is no longer zero

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 \neq 0 \qquad (5.27)$$

the distribution itself being of the form shown in Fig. 5.2. This means that in a large number of experiments, all carried out on identical systems, we would obtain two values of E, namely E_1 and E_2, their frequency of occurrence being respectively proportional to a_1^2 and a_2^2.

8

Thus, although the energy of a system in a composite state is still time-independent, it is no longer single-valued as it was for a system in a stationary state. However, a suitable experiment still forces the energy to assume one of its eigenvalues, except that now this eigenvalue can be either E_1 or E_2.
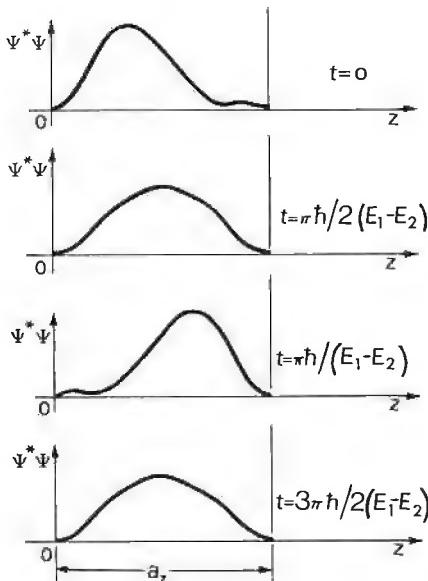
Fig. 5.4. The probability density function $\Psi^*\Psi$ for the lowest composite state of a particle confined in an infinitely deep one-dimensional potential well; $a_1^2 = 0.90$, $a_2^2 = 0.10$.

Let us now inquire into the position and momentum of the particle. Again substituting from (5.22) we obtain

$$\langle z \rangle = \int \Psi^* z \Psi \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} \left(a_1^2 z \sin^2 \frac{\pi z}{a_z} + a_2^2 z \sin^2 \frac{2\pi z}{a_z} \right.$$

$$\left. + 2a_1 a_2 z \sin \frac{\pi z}{a_z} \sin \frac{2\pi z}{a_z} \cos \frac{E_1 - E_2}{\hbar} t \right) dz$$

$$= \frac{1}{2} a_z \left(a_1^2 + a_2^2 - \frac{64}{9\pi^2} a_1 a_2 \cos \frac{3\pi^2 \hbar}{2ma_z^2} t \right) \qquad (5.28)$$

$$\langle z^2 \rangle = \int \Psi^* z^2 \Psi \, dz$$

$$= \frac{2}{a_z} \int_0^{a_z} \left(a_1^2 z^2 \sin^2 \frac{\pi z}{a_z} + a_2^2 z^2 \sin^2 \frac{2\pi z}{a_z} \right.$$

$$\left. + 2a_1 a_2 z^2 \sin \frac{\pi z}{a_z} \sin \frac{2\pi z}{a_z} \cos \frac{E_1 - E_2}{\hbar} t \right) dz$$

$$= \frac{1}{3} a_z^2 \left\{ a_1^2 \left(1 - \frac{3}{2\pi^2} \right) + a_2^2 \left(1 - \frac{3}{8\pi^2} \right) - \frac{32}{3\pi^2} a_1 a_2 \cos \frac{3\pi^2 \hbar}{2ma_z^2} t \right\} \quad (5.29)$$

so that now the variance of the position variable becomes a function of time

$$\sigma_z^2 = \langle z^2 \rangle - \langle z \rangle^2 = f(t) \quad (5.30)$$

Similarly, for the linear momentum of the particle we obtain

$$\langle p \rangle = \int \Psi^* \left(-j\hbar \frac{\partial}{\partial z} \right) \Psi \, dz$$

$$= -j\hbar \frac{2}{a_z} \int_0^{a_z} \left(a_1^* \sin \frac{\pi z}{a_z} e^{jE_1 t/\hbar} + a_2^* \sin \frac{2\pi z}{a_z} e^{jE_2 t/\hbar} \right)$$

$$\times \left(a_1 \frac{\pi}{a_z} \cos \frac{\pi z}{a_z} e^{-jE_1 t/\hbar} + a_2 \frac{2\pi}{a_z} \cos \frac{2\pi z}{a_z} e^{-jE_2 t/\hbar} \right) dz$$

$$= 0 \quad (5.31)$$

$$\langle p^2 \rangle = \int \Psi^* \left(-\hbar^2 \frac{\partial^2}{\partial z^2} \right) \Psi \, dz$$

$$= \hbar^2 \frac{2}{a_z} \int_0^{a_z} \left(a_1^* \sin \frac{\pi z}{a_z} e^{jE_1 t/\hbar} + a_2^* \sin \frac{2\pi z}{a_z} e^{jE_2 t/\hbar} \right)$$

$$\times \left(a_1 \frac{\pi^2}{a_z^2} \sin \frac{\pi z}{a_z} e^{-jE_1 t/\hbar} + a_2 \frac{4\pi^2}{a_z^2} \sin \frac{2\pi z}{a_z} e^{-jE_2 t/\hbar} \right) dz$$

$$= \frac{\pi^2 \hbar^2}{a_z^2} (a_1^2 + 4a_2^2) \quad (5.32)$$

so that the variance of the momentum variable is given by

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \frac{\pi^2 \hbar^2}{a_z^2} (a_1^2 + 4a_2^2) \quad (5.33)$$

The variance σ_p^2 is not time-dependent however, since the corresponding probability distribution A^*A does not depend on time either, as can be seen from Fig. 5.5 (see also problem 8). This short exercise shows that when the system is in a composite energy state, the mean value and

variance of its position variable become time-dependent, though this does not apply to all the variables. This dependence is a direct result of the fact that the probability density function (5.24) is now a function of time.
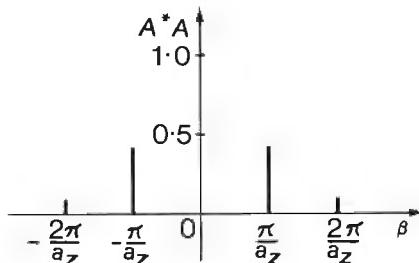

Fig. 5.5. The function $A*A$ for a particle in an infinitely deep potential well, the system being in its lowest composite energy state; $a_1^2 = 0.90$, $a_2^2 = 0.10$.

This argument would seem to suggest the following thought: whenever the movement of a bound particle can be observed within the system, the corresponding wave function must consist of more than a single energy eigenfunction. This state of affairs should not surprise us since, according to (3.66), the position observable $\langle z \rangle$ must involve $\Psi^*\Psi$, and if $\langle z \rangle$ varies with time, so must $\Psi^*\Psi$. Thus, if there is any information available concerning temporal variations of the position of the particle within the system, this fact alone indicates straight away that the system is in a composite state and that the corresponding wave function must contain at least two different energy eigenfunctions. The more we approach the idea of a classical particle, the further we move away from a pure energy eigenstate. The wave packet consisting, according to (3.19), of a large number of eigenfunctions and representing a free particle is a good example of this process. A bound particle in a stationary state certainly does not resemble the point particle of classical mechanics.

5.5. Expansion in terms of eigenfunctions

Let us now generalize the problem of the last section and assume that the dynamic state of a system is characterized by a wave function of the form $\Psi = \Psi(z, t)$. We can then show[3,4] that, due to the orthogonal properties of the eigenfunctions, this more general wave function $\Psi(z, t)$ can be constructed from a number, if need be an infinite number, of, say, energy eigenfunctions of the system. This process is quite similar to the Fourier synthesis of an arbitrary periodic function in terms of the fundamental and its harmonics, except that it is more general. Let us then assume that the wavefunction $\Psi(z, t)$ can be represented at a given time $t = t_0$ by an infinite series of time-dependent energy eigenfunctions Ψ_n

$$\Psi(z, t_0) = \sum_n a_n(t_0)\Psi_n(z, t_0) \tag{5.34}$$

As usual, we can find the coefficients $a_n(t_0)$ by multiplying both sides of (5.34) by $\Psi^*(z, t_0)$ and integrating term by term; this gives

$$a_n(t_0) = \int \Psi_n^*(z, t_0)\Psi(z, t_0)\,\mathrm{d}z \tag{5.35}$$

We now ask whether the $a_n(t_0)$ derived for a given instant of time $t = t_0$ are the same for any other t, or whether they vary with time. We can answer this question by assuming that (5.34) is valid for any t, substituting the series into Schrödinger's equation and then comparing both sides of the equation term by term. Writing Schrödinger's equation in the form (3.65a), we obtain

$$\hat{H}\Psi = j\hbar\frac{\partial}{\partial t}\Psi \tag{5.36}$$

Substituting (5.34) in (5.36) and putting t for t_0 both in Ψ and in Ψ_n, but not in a_n, we obtain

$$\sum_n a_n(t_0)\hat{H}\Psi_n(z, t) = \sum_n a_n(t_0)E_n\Psi_n(z, t) \tag{5.37}$$

for conservative systems, since then $\Psi_n(z, t)$ is of the form (4.16). But (5.37) reduces to an identity, term by term, if we bear in mind the definition of the eigenfunctions Ψ_n,

$$\hat{H}\Psi_n(z, t) = E_n\Psi_n(z, t) \tag{5.38}$$

This shows that as long as we are dealing with a conservative system ($\hat{H}$ independent of t), $a_n(t) = a_n(t_0)$ and a single choice of the coefficients a_n is sufficient to represent the system and the wave function $\Psi(z, t)$ for as long as we wish. Although $\Psi(z, t)$ will vary with time, since the different eigenfunctions Ψ_n all 'beat' with each other, the coefficients a_n remain constant. We shall see in chapter 7 that the situation becomes radically different for $\hat{H} = \hat{H}(t)$, when the system is no longer conservative, but begins to exchange energy with the outside world.

Problems

1. Consider the three-dimensional potential well of chapter 4. Quote degenerate states additional to those mentioned in the text. What is the difference between the two types of degeneracy? Which type of degeneracy is easier to spot?

2. Write the first few degenerate states for a particle in an infinitely deep potential well which has $a_x = a_y \neq a_z$. What would happen if we made $a_z = 2a_x$?

3. Consider a particle in an infinitely deep potential well of one dimension. Calculate the integrals $\int \Psi_m^*\Psi_n\,\mathrm{d}z$ for $m = n$ and $m \neq n$ where $m = 1, 2, 3$.

4. Carry out calculations similar to those described in the previous problem for the first two energy states of a hydrogen atom. What do you conclude?

5. Show by a straightforward substitution that (5.3) is a solution of Schrödinger's equation provided that Ψ_m and Ψ_n are.

6. Show for $n = 3$ that the normalization of Ψ imposes the condition described by (5.7). Try to show by mathematical induction that $\sum_n a_n^* a_n = 1$ as $n \to \infty$.

7. Consider a classical particle moving along the flat bottom of an infinitely deep potential well. Calculate $\langle z \rangle$, $\langle p \rangle$, σ_z and σ_p for such a particle, assuming that the kinetic energy of the particle is E. The walls of the well are assumed to be perfectly elastic.

8. Find the probability distribution A^*A for a particle bound in an infinitely deep, one-dimensional potential well, the system being in the lowest composite energy state. Is A^*A time-dependent? If not, why not? Are there any clear physical reasons for your conclusion?

References

1. H. Weyl, op. cit.
2. E. P. Wigner, *Group theory and its applications to the quantum mechanics of atomic spectra*, Academic Press, New York, 1959.
3. L. I. Schiff, op. cit.; Sections 10 and 11.
4. E. C. Kemble, *The fundamental principles of quantum mechanics*, McGraw-Hill Book Company Inc., New York, 1937; Chapter 4 and Section 30.
5. P. T. Matthews, op. cit.; Chapter 12.

6. Time-independent Perturbations

In chapter 4 we discussed at some length the concept of a bound particle and the corresponding stationary states. We also noted the fact that there is a close algebraic resemblance between the corresponding wave equations and the wave equations encountered in the discussion of resonant cavities. Although the electrical model was introduced purely for didactic reasons and not because of any physical similarity, it enabled us to accept the mathematics of the problem without too much effort and helped us to concentrate on the more difficult task of physical interpretation of the results. We will follow the same procedure in this chapter, and use the model of an electric transmission line in the discussion of slight changes or perturbations in the parameters of a quantum mechanical system and the effect such changes may have on the corresponding energy eigenvalues and eigenfunctions of a bound particle.

6.1. General considerations

In quantum mechanics, we can seldom hope to solve a problem exactly because of the complexity of the systems involved. In chapter 4 we have already discussed some of the few exact solutions, e.g., a particle in a rectangular well, harmonic oscillator and the hydrogen atom, but in the majority of cases approximate methods must be used,[1] either because the binding potential function is too complicated or because the effect of other particles has to be considered. Even in the case of a helium atom, which contains only two electrons outside its nucleus, we have to use an approximate method in order to calculate the appropriate energy eigenvalues. Fortunately, it is often possible to assume that the coupling forces between individual electrons are relatively weak so that one can first calculate the energy eigenvalues of individual electrons, possibly allowing for the space charge effect of those close to the nucleus (central field approximation) and then include the so-called Coulomb interaction forces as a form of perturbation of the original field; this leads to a new set of eigenvalues which usually differ from the old eigenvalues of the atom only slightly. One can then consider other effects, such as the spin–orbit or L–S coupling which further affects the energy eigenvalues of an atom, as already explained in section 4.6. All such effects which ultimately

lead to the fine and hyperfine structure of atomic spectra, can be calculated with the help of perturbations or other approximate methods.

For the sake of simplicity we will mostly consider one-dimensional systems; this will enable us to keep the algebra relatively simple and concentrate on the physical aspect of the problem; at the same time it makes possible the use of an electrical transmission line as a mathematical model. In this chapter, we will consider time-independent perturbations only; in practice, this usually amounts to the comparison of energy eigenvalues in two conservative systems with slightly different parameters.

6.2. Transmission line model

Let us now consider the effect of a small change in an electrical transmission line, a model simple enough to provide both exact and approximate solutions which can be compared. Figure 6.1 shows a short length l of a loss-less transmission line of characteristic impedance $Z_0 = (L/C)^{\frac{1}{2}}$ and phase constant $k = \omega(LC)^{\frac{1}{2}}$, where L and C are respectively inductance and capacitance per unit length of the line. We recall [2, 3, 4, 5] that
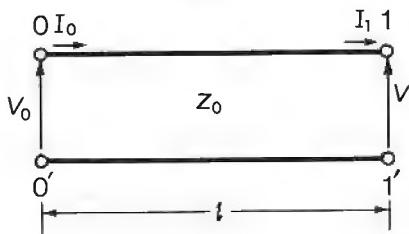
Fig. 6.1. Electric transmission line of length l and characteristic impedance Z_0.

the steady state voltage and current distribution along the line are given by the following expressions

$$V(z) = V_0 \cos kz - jZ_0 I_0 \sin kz$$

$$I(z) = -j\frac{V_0}{Z_0} \sin kz + I_0 \cos kz \tag{6.1}$$

where V and I represent the amplitudes of sinusoidal fluctuation of angular frequency ω. The two constants V_0 and I_0 in (6.1) can be determined when the power delivered by the generator and the load connected across the output terminals of the line are specified.

Now assume that the transmission line shown in Fig. 6.1 is in the state of current resonance, so that $I(z)$ is zero at both ends of the line. We find from equations (6.1) that this is possible only when

$$\tan kl = 0$$

or

$$k = \frac{n\pi}{l} = \omega_n(LC)^{\frac{1}{2}} \tag{6.2}$$

Thus, for a given set of parameters l, L, and C, this type of resonance can only occur at frequencies given by (6.2) where $n = 1, 2, 3, \ldots$ and is equal to the number of half wavelengths along the line.

Following this simple introduction, let us now assume that the transmission line suffers a sudden change in the value of one of its parameters near the end, say between $z = z_1$ and $z = l$, where $l - z_1 = \delta \ll l$, as shown in Fig. 6.2. After some algebraic manipulation, which amounts to making the current and voltage continuous across the junction of the two sections
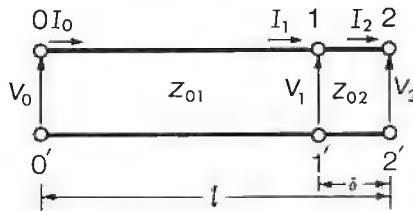
Fig. 6.2. Modified electric transmission line of length l.

of the line, we find that now the following expressions represent the voltage and current distributions along the line

$$V(z) = V_0 \cos k_1 z - jZ_{01}I_0 \sin k_1 z$$

$$I(z) = -j\frac{V_0}{Z_{01}} \sin k_1 z + I_0 \cos k_1 z \tag{6.3}$$

for $\quad 0 \leqslant z \leqslant z_1$

$$V(z) = V_0 \left\{ \cos k_1 z_1 \cos k_2(z - z_1) - \frac{Z_{02}}{Z_{01}} \sin k_1 z_1 \sin k_2(z - z_1) \right\}$$

$$- jI_0\{Z_{01} \sin k_1 z_1 \cos k_2(z - z_1) + Z_{02} \cos k_1 z_1 \sin k_2(z - z_1)\}$$

$$I(z) = -jV_0 \left\{ \frac{1}{Z_{02}} \cos k_1 z_1 \sin k_2(z - z_1) + \frac{1}{Z_{01}} \sin k_1 z_1 \cos k_2(z - z_1) \right\}$$

$$+ I_0 \left\{ -\frac{Z_{01}}{Z_{02}} \sin k_1 z_1 \sin k_2(z - z_1) + \cos k_1 z_1 \cos k_2(z - z_1) \right\}$$

$$\tag{6.4}$$

for $\quad z_1 \leqslant z \leqslant l$

where

$$k_1 = \omega(L_1 C_1)^{\frac{1}{2}}, \qquad k_2 = \omega(L_2 C_2)^{\frac{1}{2}}$$

$$Z_{01} = (L_1/C_1)^{\frac{1}{2}}, \qquad Z_{02} = (L_2/C_2)^{\frac{1}{2}} \tag{6.5}$$

The subscripts 1 and 2 in (6.5) refer to the two sections of the line shown in Fig. 6.2, respectively.

The resonance condition is now specified by putting $I_0 = I_2 = 0$, when we find from the second equation of (6.4) that

$$\frac{Z_{01}}{Z_{02}} = -\frac{\tan k_1 z_1}{\tan k_2(l - z_1)} \qquad (6.6)$$

Since k_1 and k_2 are both functions of ω, (6.6) gives us those angular frequencies ω_n at which the current resonance occurs for any given set of parameters k_1, k_2, Z_{01}, and Z_{02}. In the two extreme cases of $z_1 = l$ and $z_1 = 0$, (6.6) reduces to (6.2).

For reasons which will become clear later, let us now make the problem less general by requiring continuity of $dI(z)/dz$ at the junction as well as continuity of $I(z)$. Calculating dI/dz from both (6.3) and (6.4) and making the two expressions equal at $z = z_1$, we obtain a new constraint, namely

$$\frac{Z_{01}}{Z_{02}} = \frac{k_1}{k_2} \qquad (6.7)$$

For a loss-less transmission line this imposes the condition $C_1 = C_2$ although not $L_1 = L_2$. (The same conclusion can be deduced more simply by directly considering the transmission line equations $dV/dz = -j\omega LI$ and $dI/dz = -j\omega CV$ at the point $z = z_1$.) Substituting (6.7) in (6.6) we obtain

$$\frac{k_1}{k_2} = -\frac{\tan k_1 z_1}{\tan k_2(l - z_1)} \qquad (6.8)$$

which is a transcendental equation and describes the condition of current resonance of the composite transmission line shown in Fig. 6.2. We can solve (6.8) for any given set of k_1, k_2, l, and z_1/l, each choice of parameters giving us an infinite number of roots or angular frequencies ω_n at which the resonance can occur, the number of corresponding half wavelengths between the terminals being given by n. Figure 6.3 shows the result of such calculations for $k_2^2 = 1.1 k_1^2$, $l(L_1 C_1)^{\frac{1}{2}} = 1$ sec, ω_n being shown as a function of $(l - z_1)/l = \delta/l$, $0 \leqslant \delta/l \leqslant 1$. Knowing δ/l we can read directly from Fig. 6.3 the corresponding values of ω_n. However, we must note that even in this simple case the equation defining the resonance condition is transcendental, its solution being somewhat laborious. This situation rapidly deteriorates in the case of more complicated systems when clearly some approximate and general procedure for calculating the resonance condition becomes desirable. Such a method will be described in section 6.3, but in order to assess its accuracy we must first obtain an approximate expression for ω_n in the particular case of (6.8), assuming that $(l - z_1)/l = \delta/l \ll 1$.

Anticipating our future requirements let us change the notation as follows: the resonant frequencies obtained from (6.2) and referring to the 'unperturbed' transmission line of Fig. 6.1, will be called ω_n^0; the corresponding resonant frequencies of the 'perturbed' line of Fig. 6.2, which are solutions of (6.8), will be called ω_n, the difference between the two for any given resonance n being indicated by a primed symbol $\omega_n' = \omega_n - \omega_n^0$.
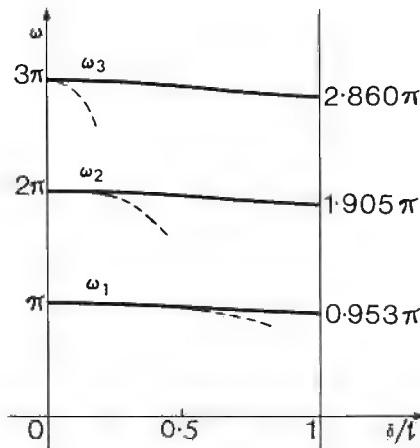

Fig. 6.3. Resonant frequency ω as a function of δ/l; broken line shows the approximate solution.

Similarly, the parameters of the unperturbed line will be L^0 and C^0, with $k^0 = \omega^0 (L^0 C^0)^{\frac{1}{2}} = \omega^0 \tau^0$, and those of the perturbed line will be $k_1 = \omega (L^0 C^0)^{\frac{1}{2}} = \omega \tau^0 = (\omega^0 + \omega') \tau^0$ and $k_2 = \omega (LC)^{\frac{1}{2}} = \omega \tau = (\omega^0 + \omega') \tau$. Furthermore, since the condition of continuity of slope, (6.7), requires $C^0 = C$, we obtain $\tau^2 = \tau^{02} + \tau^{02}(L'/L^0)$, where $L' = L - L^0$, so that, to the first order of approximation

$$\frac{\tau^2}{\tau^{02}} - 1 = \frac{L'}{L^0} \approx 1 - \frac{\tau^{02}}{\tau^2} \tag{6.9}$$

We can now rewrite (6.8) as

$$\tan \{\pi - \omega \tau^0 (l - \delta)\} = \frac{\tau^0}{\tau} \tan \omega \tau \delta \tag{6.10}$$

bearing in mind that $-\tan x = \tan (\pi - x)$. Solving for the left-hand side of (6.10) and remembering that, for small values of the argument, $\tan^{-1} x \approx x - \frac{1}{3}x^3 + \cdots$ and $\tan x \approx x + \frac{1}{3}x^3 - \cdots$, we obtain for the lowest

resonant frequency ($n = 1$),

$$\pi - \omega^0 \tau^0 l - \omega' \tau^0 l + \omega \tau^0 \delta = \tan^{-1} \left\{ \frac{\tau^0}{\tau} \tan \omega \tau \delta \right\}$$

$$\approx \frac{\tau^0}{\tau} \tan \omega \tau \delta - \frac{1}{3} \left(\frac{\tau^0}{\tau} \right)^3 \tan^3 \omega \tau \delta$$

$$\approx \frac{\tau^0}{\tau} \omega \tau \delta + \frac{1}{3} \frac{\tau^0}{\tau} \omega^3 \tau^3 \delta^3 - \frac{1}{3} \left(\frac{\tau^0}{\tau} \right)^3 \omega^3 \tau^3 \delta^3 \quad (6.11)$$

The first two terms on the left-hand side of (6.11) cancel out in view of the resonance condition (6.2), ω^0 being the unperturbed angular frequency. The fourth term on the left-hand side is identical with the first term on the right-hand side, so that they also cancel and we are left with

$$\omega' \tau^0 l \approx -\frac{1}{3} \frac{\tau^0}{\tau} \left(1 - \frac{\tau^{02}}{\tau^2} \right) \omega^3 \tau^3 \delta^3 \quad (6.12)$$

Dividing both sides of (6.12) by $\tau^0 l$, substituting from (6.9) and putting $\omega \tau \approx \omega^0 \tau^0 = \pi/l$ from (6.2), we obtain, finally,

$$\omega' = -\frac{1}{3} \omega^0 \frac{L'}{L^0} \pi^2 \frac{\delta^3}{l^3} \quad (6.13)$$

This equation gives the change in the resonant frequency ω' in terms of the original or unperturbed resonant frequency ω^0 and the line parameters L'/L^0 and δ/l, as shown by the lowest dashed curve in Fig. 6.3. We can now see that this curve agrees quite well with the continuous curve obtained from (6.8), as long as δ/l is less than, say, 0·2, both curves being calculated for the same choice of the line parameters.

6.3. Perturbation method applied to the transmission line problem

Let us now consider a more general approach to the problem of calculating the resonant frequency ω_n of the composite transmission line shown in Fig. 6.2. We know from the simple theory[2, 3, 4, 5] that both transmission line equations are of the first order and can be combined to give a single differential equation of the second order, either in $V = V(z)$ or in $I = I(z)$. If both I and dI/dz are made continuous everywhere along the line, as they have been in our example, the corresponding second order equation for the current distribution $I = I(z)$, which must be satisfied in the whole interval $0 \leqslant z \leqslant l$, is

$$\frac{d^2 I}{dz^2} + \omega^2 LCI = 0 \quad (6.14)$$

Dividing both sides of (6.14) by LC we obtain

$$\hat{O}I = OI \quad (6.15)$$

where $\hat{O} = -(1/LC)\,\mathrm{d}^2/\mathrm{d}z^2$ is an operator and $O = \omega^2$ are its eigenvalues, (6.15) being an eigenvalue equation of the type (3.65) discussed in chapter 3.

For the unperturbed line, Fig. 6.1, we have $\hat{O}^0 = -(1/L^0C^0)\,\mathrm{d}^2/\mathrm{d}z^2$ having eigenvalues, from (6.2),

$$O_n^0 = \omega_n^{02} = \frac{n^2\pi^2}{l^2L^0C^0} = \frac{n^2\pi^2}{l^2\tau^{02}} \tag{6.16}$$

which give the corresponding resonant frequencies ω_n^0. We find from (6.1), (6.15) and the appropriate boundary conditions that

$$\hat{O}^0 I_n^0 = O_n^0 I_n^0 \tag{6.17}$$

where

$$I_n^0 = -j\frac{V_0}{Z_0^0}\sin k_n^0 z = -j\frac{V_0}{Z_0^0}\sin\frac{n\pi}{l}z \tag{6.18}$$

and are the eigenfunctions belonging to the operator $\hat{O}^0$. If the parameters at one end of the line are now altered by a small amount, as is shown in Fig. 6.2, the new operator will no longer be $\hat{O}^0$ but $\hat{O} = \hat{O}^0 + \hat{O}'$, where

$$\hat{O}' = -\left(\frac{1}{LC} - \frac{1}{L^0C^0}\right)\frac{\mathrm{d}^2}{\mathrm{d}z^2}$$

$$= \left(\frac{1}{\tau^{02}} - \frac{1}{\tau^2}\right)\frac{\mathrm{d}^2}{\mathrm{d}z^2} \tag{6.19}$$

the eigenvalues of $\hat{O}$ being O_n instead of O_n^0. This leads to a new set of solutions or eigenfunctions I_n in place of I_n^0. However, if the change is small, we can rewrite (6.15), which is linear, in the following form

$$(\hat{O}^0 + \hat{O}')(I_n^0 + I_n') = (O_n^0 + O_n')(I_n^0 + I_n') \tag{6.20}$$

Carrying out the multiplications indicated in (6.20), noting the equality of the zero order terms indicated by (6.17) and retaining first order terms only (i.e., neglecting all products of the primed quantities) we obtain

$$\hat{O}^0 I_n' + \hat{O}' I_n^0 = O_n^0 I_n' + O_n' I_n^0 \tag{6.21}$$

However, we have seen in section 5.2 that, in general, the eigenfunctions form an orthogonal set, so that

$$\int I_m^{0*} I_n^0\,\mathrm{d}z = A^2 \quad \text{when} \quad m = n$$

$$= 0 \quad \text{when} \quad m \neq n \tag{6.22}$$

In our simple case, this can easily be checked by substituting (6.18) in (6.22) and integrating over the whole length of the transmission line,

i.e., between $z=0$ and $z=l$; we then obtain, for example,

$$\frac{V_0^2}{Z_0^{02}} \int_0^l \sin^2 \frac{n\pi}{l} z \, dz = \tfrac{1}{2} l \frac{V_0^2}{Z_0^{02}} = A^2 \qquad (6.23)$$

for $m=n$ and zero whenever $m \neq n$. We have also mentioned in section 5.5 that such orthogonal sets of functions can be used for expressing other wave functions over the same interval, just as in the case of Fourier series. In fact, our eigenfunctions (6.18) form a special case of a Fourier series with the cosine terms missing. Thus, in general, we can express the correction I_n' to the nth eigenfunction I_n^0 in terms of the eigenfunctions I_i^0 with suitably adjusted coefficients. For the simple case of Fig. 6.2; this amounts to expressing the correction function I_n' as a Fourier series of the form

$$I_n' = \sum_i a_i^{(n)} I_i^0 \qquad (6.24)$$

Now, using (6.24) and (6.17), the two terms of (6.21) containing I_n' can be expressed in the form

$$\hat{O}^0 I_n' = \hat{O}^0 \sum_i a_i^{(n)} I_i^0 = \sum_i a_i^{(n)} \hat{O}^0 I_i^0 = \sum_i a_i^{(n)} O_i^0 I_i^0 \qquad (6.25)$$

$$O_n^0 I_n' = O_n^0 \sum_i a_i^{(n)} I_i^0 = \sum_i a_i^{(n)} O_n^0 I_i^0 \qquad (6.26)$$

and after some rearrangement of terms (6.21) can be written as

$$\sum_i a_i^{(n)} (O_i^0 - O_n^0) I_i^0 = O_n' I_n^0 - \hat{O}' I_n^0 \qquad (6.27)$$

Multiplying both sides of (6.27) by I_k^{0*} and integrating, we obtain

$$\sum_i a_i^{(n)} (O_i^0 - O_n^0) \int I_k^{0*} I_i^0 \, dz = O_n' \int I_k^{0*} I_n^0 \, dz - \int I_k^{0*} \hat{O}' I_n^0 \, dz \quad (6.28)$$

When $k=n$, the left-hand side of (6.28) is always equal to zero bearing in mind the orthogonal property of the eigenfunctions I_n^0, so that

$$O_n' A^2 = \int I_n^{0*} \hat{O}' I_n^0 \, dz$$

or

$$O_n' = \frac{1}{A^2} \int I_n^{0*} \hat{O}' I_n^0 \, dz$$

$$= \frac{1}{A^2} O_{nn}' \qquad (6.29)$$

A^2 being the normalization constant. Since

$$O'_n = O_n - O_n^0 = \omega_n^2 - \omega_n^{02}$$
$$= (\omega_n^0 + \omega_n')^2 - \omega_n^{02}$$
$$\approx 2\omega_n'\omega_n^0$$

we obtain for the frequency correction

$$\omega_n' = \frac{O'_n}{2\omega_n^0} = \frac{1}{2\omega_n^0 A^2} O'_{nn} \tag{6.30}$$

Equations (6.29) and (6.30) give the correction to the eigenvalue O_n^0 or to the resonant frequency ω_n^0 which is required when we go over from the unperturbed transmission line shown in Fig. 6.1, to the composite or perturbed transmission line shown in Fig. 6.2.

If $k \neq n$ in (6.28), then the integral on the left-hand side is different from zero only for $i = k$. The first integral on the right-hand side now disappears altogether and we get

$$a_k^{(n)}(O_k^0 - O_n^0)A^2 = -\int I_k^{0*}O'I_n^0 \, dz = -O'_{kn}$$

or

$$a_k^{(n)} = \frac{O'_{kn}}{A^2(O_n^0 - O_k^0)} \tag{6.31}$$

Thus, from (6.24) the coefficient of the kth term $a_k^{(n)}$ in the Fourier expansion of the correction function I'_n is given by (6.31). When $k = n$ the corresponding coefficient $a_n^{(n)}$ must be zero so that the new eigenfunctions I_n still satisfy the normalization integral (6.22), the products of the coefficients $a_k^{(n)}$ being of the second order of magnitude and thus negligible.

Having obtained the general expressions for the first order corrections to the eigenfunctions (6.31), we can now recalculate the simple case of a perturbed transmission line, Fig. 6.2, and compare the results with those obtained on the basis of the exact solution. Substituting in (6.29) from (6.18) and (6.19) and bearing in mind that $\hat{O}' = 0$ between $z = 0$ and $z = z_1$ and is different from zero only between $z = z_1$ and $z = l$, we obtain

$$O'_n = \frac{1}{A^2} \int I^{0*}\hat{O}'I^0 \, dz$$
$$= \frac{2}{l} \int_{z_1}^{l} \sin \frac{n\pi}{l} z \left(\frac{1}{\tau^{02}} - \frac{1}{\tau^2} \right) \frac{d^2}{dz^2} \left(\sin \frac{n\pi}{l} z \right) dz$$
$$= -\frac{2}{l} \left(\frac{1}{\tau^{02}} - \frac{1}{\tau^2} \right) \frac{n^2\pi^2}{l^2} \int_{z_1}^{l} \sin^2 \frac{n\pi}{l} z \, dz$$

$$= -\frac{2}{l}\left(\frac{1}{\tau^{02}}-\frac{1}{\tau^2}\right)\frac{n\pi}{l}\frac{1}{2}\left(n\pi-\frac{n\pi}{l}z_1+\frac{1}{2}\sin\frac{2n\pi}{l}z_1\right)$$

$$= -\frac{1}{l}\left(\frac{1}{\tau^{02}}-\frac{1}{\tau^2}\right)\frac{n^2\pi^2}{l^2}\left(\delta-\frac{l}{2n\pi}\sin\frac{2n\pi}{l}\delta\right)$$

$$= -O_n^0\left(1-\frac{\tau^{02}}{\tau^2}\right)\left(\frac{\delta}{l}-\frac{1}{2n\pi}\sin\frac{2n\pi}{l}\delta\right) \tag{6.32}$$

For small values of $2n\pi\delta/l$ the second term in (6.32) can be expanded as a series and the correction ω_n' to the resonant frequency, from (6.30), becomes equal to

$$\omega_n' = \frac{O_n'}{2\omega_n^0} = -\frac{1}{2}\omega_n^0\left(1-\frac{\tau^{02}}{\tau^2}\right)\left(\frac{\delta}{l}-\frac{1}{2n\pi}\sin\frac{2n\pi}{l}\delta\right)$$

$$\approx -\frac{1}{2}\omega_n^0\left(1-\frac{\tau^{02}}{\tau^2}\right)\frac{2}{3}\pi^2n^2\frac{\delta^3}{l^3}$$

$$\approx -\frac{1}{3}\omega_n^0\frac{L'}{L^0}\pi^2n^2\frac{\delta^3}{l^3} \tag{6.33}$$

This is the same as (6.13) for $n=1$ and clearly shows that the perturbation method gives the same result as the previous approximation to the exact solution. One point should be noted in connection with (6.33); the neglect of higher order terms means that for a given δ/l the accuracy decreases as n increases, as shown in Fig. 6.3, the most reliable results being obtained for the fundamental frequency ω_1^0.

Let us now consider a typical coefficient of the Fourier expansion given by (6.31). Substituting again from (6.19) and bearing in mind that $O_n^0=n^2O_1^0$ (see (6.2)), we obtain

$$a_k^{(n)} = \frac{1}{A^2(O_n^0-O_k^0)}\int_{z_1}^l I_k^0{}^*\hat{O}'I_n^0\,dz$$

$$= -\frac{2}{l(k^2-n^2)O_1^0}\int_{z_1}^l \sin\frac{k\pi}{l}z\left(\frac{1}{\tau^{02}}-\frac{1}{\tau^2}\right)\frac{d^2}{dz^2}\left(\sin\frac{n\pi}{l}z\right)dz$$

$$= \frac{2}{l(k^2-n^2)\omega_1^{02}}\left(\frac{1}{\tau^{02}}-\frac{1}{\tau^2}\right)\frac{n^2\pi^2}{l^2}\int_{z_1}^l \sin\frac{k\pi}{l}z\sin\frac{n\pi}{l}z\,dz$$

$$= \frac{1}{l(k^2/n^2-1)}\left(\frac{1}{\tau^{02}}-\frac{1}{\tau^2}\right)\tau^{02}\left\{\frac{\sin(k+n)\pi z_1/l}{(k+n)\pi/l}-\frac{\sin(k-n)\pi z_1/l}{(k-n)\pi/l}\right\}$$

$$= \frac{(-1)^{k+n}}{k^2/n^2-1}\left(1-\frac{\tau^{02}}{\tau^2}\right)\left\{\frac{\sin(k-n)\pi\delta/l}{(k-n)\pi}-\frac{\sin(k+n)\pi\delta/l}{(k+n)\pi}\right\} \tag{6.34}$$

For small values of the argument $(k \pm n)\pi\delta/l$, i.e., for the first one or two correction terms of the fundamental or the second harmonic, we can use the usual approximate expression $\sin x \approx x - \frac{1}{6}x^3 + \cdots$ and write

$$a_k^{(n)} \approx (-1)^{k+n} \frac{2kn^3}{k^2 - n^2} \frac{L'}{L^0} \frac{1}{3} \frac{\pi^2\delta^3}{l^3} \tag{6.35}$$

but the accuracy of this expression drops rapidly with n, the effect of any given perturbation L'/L^0 and δ/l increasing with n. This means that, relatively speaking, a certain high harmonic n may be perturbed much more than the fundamental by changing the conditions over a small fraction of the length of the transmission line. This is physically quite understandable, because the electrical length of the line in terms of the wavelength λ_n increases with ω for a given δ/l, so that $\delta/l = \lambda_1^0/10$ for the fundamental, becomes $\delta/l = \lambda_5^0/2$ for the fifth harmonic. On the other hand, if by some coincidence $(k - n)\pi\delta/l = m\pi$, the $a_k^{(n)}$ and $a_n^{(k)}$ terms will be identically equal to zero, since one node of either mode would then coincide with $z = z_1$, no coupling due to the perturbation being possible between such modes.

It should be noted that, although (6.29) and (6.31) have been derived with the help of a transmission line model, their validity is quite general, since in fact they are based on the general eigenvalue equation (6.15). When used in quantum mechanics, the only difference is that the corresponding eigenfunctions are always normalized to unity so that $A^2 = 1$, an assumption which would not apply to the transmission line model. Also we find from (6.15), (6.20), and the following transformations that in the case of a three-dimensional system (6.29), (6.31) would still be valid except that now the integrals with respect to z would have to be converted into triple integrals with respect to x, y, and z.

We may now ask what are the advantages of the perturbation method. The most important is that in a large number of cases it is the only method which can be used to get any results at all. As we have already mentioned, most problems in quantum mechanics are so complex, that exact solutions cannot be contemplated and approximate procedures are required. Another advantage of the perturbation method is that it is quite general, and to a large extent, independent of the particular set of boundary conditions. Also it provides not only the corrections to the eigenvalues O_n or ω_n but, at the same time, the coefficients of the series expansion in terms of the eigenfunctions I_n^0 of the correction functions I_n'. In this way, we obtain all the necessary information concerning a new, perturbed, system expressed in terms of the parameters of some simpler, unperturbed, system. Finally, the perturbation method brings out one more point, which is of some importance in quantum mechanics. Since

the operator $O = O^0 + O'$ is linear, we can write

$$
\begin{aligned}
I_1 &= & I_1^0 + a_2^{(1)} I_2^0 + a_3^{(1)} I_3^0 + \cdots \\
I_2 &= a_1^{(2)} I_1^0 + & I_2^0 + a_3^{(2)} I_3^0 + \cdots \\
I_3 &= a_1^{(3)} I_1^0 + a_2^{(3)} I_2^0 + & I_3^0 + \cdots \\
&\quad\vdots \quad\quad \vdots \quad\quad \vdots \quad\quad \vdots
\end{aligned}
\tag{6.36}
$$

or, using matrix notation,

$$
\begin{bmatrix} I_1 \\ I_2 \\ I_3 \\ \vdots \end{bmatrix}
=
\begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix}
\begin{bmatrix} I_1^0 \\ I_2^0 \\ I_3^0 \\ \vdots \end{bmatrix}
+
\begin{bmatrix} 0 & a_2^{(1)} & a_3^{(1)} & \cdots \\ a_1^{(2)} & 0 & a_3^{(2)} & \cdots \\ a_1^{(3)} & a_2^{(3)} & 0 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix}
\begin{bmatrix} I_1^0 \\ I_2^0 \\ I_3^0 \\ \vdots \end{bmatrix}
\tag{6.36}
$$

where now the eigenfunctions form a column matrix or an n-dimensional vector and are operated on by an $n \times n$ matrix, n tending to infinity. The fact that the perturbation of a system can be expressed so readily in terms of matrices is not a coincidence and is related to the so-called matrix representation of quantum mechanics discussed in section 7.5, and first suggested by Heisenberg.[6] The notation of [6.36] shows rather well that the main effect of a perturbation is to alter the modes or eigenfunctions of the original system by introducing small admixtures of other modes or eigenfunctions, as is clearly shown by the presence of the off-diagonal terms in the second matrix. This situation is quite common in electrical engineering both in the theory of networks and in connection with wave-guides and microwave cavities. In fact, the usual method of tuning a microwave cavity with the help of a screw or a depression in its wall causes the required change in the eigenvalues and eigenfunctions of the system.

6.4. Particle in a modified, infinitely deep, one-dimensional potential well

We are now ready to consider a simple quantum mechanical problem, the case of a particle bound in a modified, infinitely deep potential well. As before we will first derive an exact solution of the problem and then, in section 6.5, apply the approximate, but quite general perturbation method developed in section 6.3.

Figure 6.4 shows the geometry of an infinitely deep, one-dimensional potential well. This simple case has already been discussed in chapters 4 and 5, where equations (5.11) and (5.12) give, for a well of width l, the

wave functions and energy eigenvalues:

$$\Psi_n = \left(\frac{2}{l}\right)^{\frac{1}{2}} \sin kz \, e^{-jE_{nt}/\hbar} \tag{6.37}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ml^2} \tag{6.38}$$

where

$$k^2 = \frac{n^2\pi^2}{l^2} \tag{6.39}$$
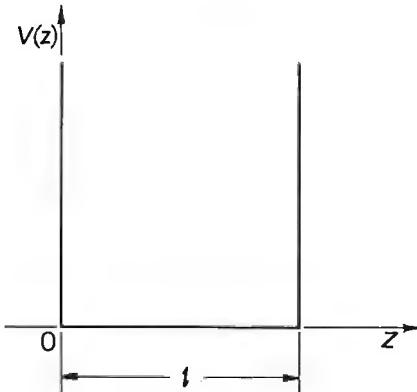
Fig. 6.4. A one-dimensional, infinitely deep potential well.

Let us now assume that the potential function $V = V(z)$ is no longer zero everywhere inside the potential well but has a small depression near one end, as shown in Fig. 6.5, where $V = -V_0$. This simple model represents the possible effect of another particle, such as a neutron, occupying a small region near one end of the potential well. Substituting the new values of the potential function $V(z)$ in the one-dimensional equivalent of (4.17), we obtain two time-independent Schrödinger equations;

$$\frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad \text{for} \quad 0 \leqslant z \leqslant z_1 \tag{6.40}$$

$$\frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}(E+V_0)\psi = 0 \quad \text{for} \quad z_1 \leqslant z \leqslant l \tag{6.41}$$

each equation being valid over a different interval of z. The general solutions of these equations are, by analogy with (4.8) and (4.31),

$$\psi = A_1 \cos k_1 z + B_1 \sin k_1 z \quad \text{for} \quad 0 \leqslant z \leqslant z_1 \tag{6.42}$$

$$\psi = A_2 \cos k_2 z + B_2 \sin k_2 z \quad \text{for} \quad z_1 \leqslant z \leqslant l \tag{6.43}$$

where now

$$k_1^2 = \frac{2mE}{\hbar^2}, \quad k_2^2 = \frac{2m(E+V_0)}{\hbar^2} \tag{6.44}$$

The integration constants A_1, B_1, A_2, B_2 and the phase constants k_1, k_2 can now be suitably adjusted to match the two solutions (6.42) and (6.43) at the point $z=z_1$, both in magnitude and slope. As we know, this condition is invariably required in quantum mechanics to prevent the
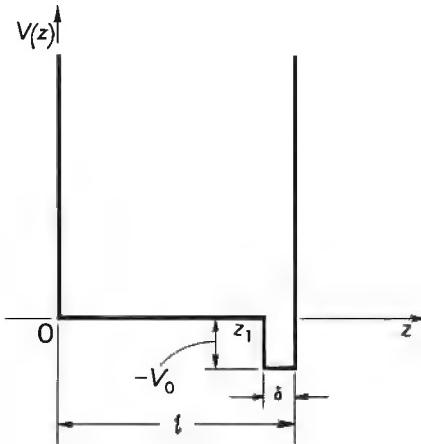
Fig. 6.5. Modified one-dimensional, infinitely deep potential well.

appearance of infinite forces or momenta, which are physically non-realizable, anywhere in the interval. Of course, the simplifying assumption of an infinitely deep potential well is also physically non-realizable, but the resulting discontinuity in the slope of the wave function only appears at the two edges of the well, i.e., at $z=0$ and $z=l$, where $\psi=0$. Substituting this last condition in (6.42) and (6.43) we obtain

$$A_1 = 0 \tag{6.45}$$

$$\frac{A_2}{B_2} = -\tan k_2 l \tag{6.46}$$

so that now

$$\psi = B_1 \sin k_1 z \quad \text{for} \quad 0 \leqslant z \leqslant z_1 \tag{6.47}$$

$$\psi = -\frac{B_2}{\cos k_2 l} \sin k_2 (l-z) \quad \text{for} \quad z_1 \leqslant z \leqslant l \tag{6.48}$$

The next step is to eliminate B_2 by using the condition that ψ must be continuous at $z=z_1$. This leads to a new expression for (6.48) given by

$$\psi = B_1 \frac{\sin k_1 z_1}{\sin k_2 (l-z_1)} \sin k_2 (l-z) \tag{6.49}$$

Finally, the last integration constant B_1 can be determined from the usual normalization condition

$$\int_0^{z_1} \psi^*\psi \, dz + \int_{z_1}^l \psi^*\psi \, dz = 1 \tag{6.50}$$

where the wave function ψ has a different algebraic form in the two integration intervals.

Using the condition of continuity of slope at the point $z = z_1$ we obtain a relationship between the two phase constants k_1 and k_2. Differentiating (6.47) and (6.49) with respect to z and equating the derivatives at $z = z_1$ we obtain

$$\frac{k_1}{k_2} = -\frac{\tan k_1 z_1}{\tan k_2 (l - z_1)} \tag{6.51}$$

which is the same as (6.8). Since both k_1 and k_2 are functions of the total energy of the particle (see (6.44)), (6.51) when solved for E gives the new energy eigenvalues of the perturbed system, for any given l, z_1, m, and V_0. Putting $l - z_1 = \delta$ as before and choosing $V_0 = 0 \cdot 1 \, E_1^0$, where the values with the superscript zero again refer to the unperturbed system of Fig. 6.4 and are given by (6.37) and (6.38), we can solve the transcendental equation (6.51) and plot its roots as a function of δ/l, where $0 \leqslant \delta/l \leqslant 1$. The results are shown in Fig. 6.6, which strongly resembles Fig. 6.3, except for some minor details which are associated with the somewhat different definition of k in terms of ω and E, as is shown by (6.5) and (6.44).

Let us now solve (6.51) approximately. Introducing again the superscript zero to denote all quantities associated with the unperturbed system shown in Fig. 6.4 we have, from (6.38), $k^{02} l^2 = 2m E_n^0 l^2 / \hbar^2 = n^2 \pi^2$. Then, using primes to denote the difference between the new, perturbed, and the old, unperturbed quantities, we have $E' = E - E^0$, so that now

$$k_1^2 = \frac{2m}{\hbar^2} (E_n^0 + E_n') = k^{02} \left(1 + \frac{E_n'}{E_n^0}\right)$$

and

$$k_2^2 = \frac{2m}{\hbar^2} (E_n^0 + V_0 + E_n') = k^{02} \left(1 + \frac{V_0 + E_n'}{E_n^0}\right)$$

Rewriting (6.51) as

$$\tan \{\pi - k_1(l - \delta)\} = \frac{k_1}{k_2} \tan k_2 \delta \tag{6.52}$$

we can now solve it approximately for small E' and δ, bearing in mind the multiplicity of roots

$$n\pi - k^0 l - \frac{1}{2} k^0 l \frac{E'_n}{E^0_n} + k_1 \delta = \tan^{-1}\left(\frac{k_1}{k_2} \tan k_2 \delta\right)$$

$$\approx \frac{k_1}{k_2} \tan k_2 \delta - \frac{1}{3}\left(\frac{k_1}{k_2}\right)^3 \tan^3 k_2 \delta$$

$$\approx \frac{k_1}{k_2}\left(k_2\delta + \frac{1}{3}k_2^3\delta^3\right) - \frac{1}{3}\left(\frac{k_1}{k_2}\right)^3 k_2^3\delta^3$$

$$\approx k_1\delta + \frac{1}{3}k_1 k_2^2\delta^3 - \frac{1}{3}k_1^3\delta^3 \qquad (6.53)$$

On the left-hand side of (6.53) the first two terms cancel because of the definition of k^0, (6.39). The last term on the left-hand side and the first on the right-hand side also cancel so that, putting $k_1 \approx k^0 = n\pi/l$, we are left with the following expression for E'_n, the correction to the nth energy
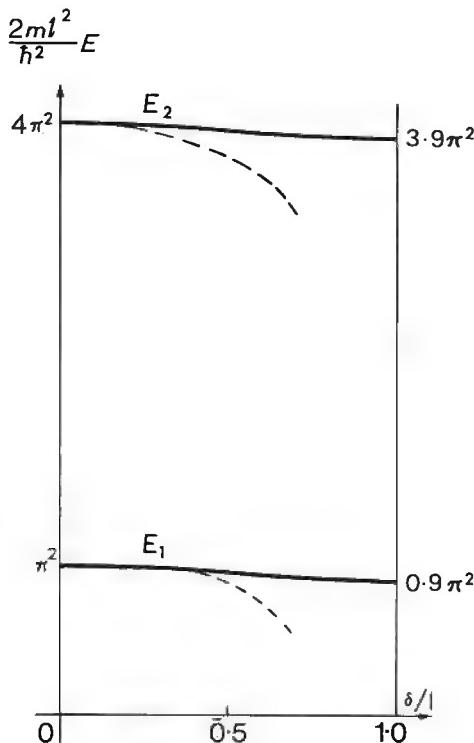
Fig. 6.6. The first two eigenvalues E_n as functions of δ/l; the broken line again shows the approximate solution.

eigenvalue of the system:

$$\frac{2m}{\hbar^2} E'_n = -\frac{2}{3} k^0 \frac{\delta^3}{l} (k_2^2 - k_1^2)k_1$$

$$\approx -\frac{2}{3} n^2 \pi^2 \frac{\delta^3}{l^3} \frac{2m}{\hbar^2} V_0$$

or, more simply,

$$E'_n = -\frac{2}{3} V_0 \pi^2 n^2 \frac{\delta^3}{l^3} \tag{6.54}$$

This expression is shown as a dashed line in Fig. 6.6 for $n = 1, 2$.

6.5. Perturbation method applied to a particle bound in a modified, infinitely deep, one-dimensional potential well

In the simple case we have just considered in section 6.4, it was possible to obtain an exact solution for a slightly modified quantum mechanical system. Such situations are very rare however and, in the majority of cases, we have to use an approximate method, such as the perturbation method developed in section 6.3. We now apply this method to the quantum mechanical problem just discussed.

A comparison of (6.14), (6.15) with (6.40), (6.41) shows that the operator $\hat{O}$ is now given by

$$\hat{O} = \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} - V_0 \tag{6.55}$$

where $\hat{H}$ is the Hamiltonian operator already discussed in chapters 3 and 4. Bearing in mind the wave equation of the unperturbed system, which has the same form as (6.40) but is valid over the whole interval $0 \leqslant z \leqslant l$, we find that the Hamiltonian operator $\hat{H}$ of (6.55) can be written as

$$\hat{H} = \hat{H}^0 + \hat{H}' \tag{6.56}$$

where

$$\hat{H}^0 = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \tag{6.57}$$

and

$$\hat{H}' = -V_0 \tag{6.58}$$

The two equations (6.40) and (6.41) can now be combined to give a single eigenvalue equation

$$\hat{H}\psi = E\psi \tag{6.59}$$

where $\hat{H} = \hat{H}^0$ for $0 \leqslant z < z_1$ and $\hat{H} = \hat{H}^0 + \hat{H}'$ for $z_1 \leqslant z \leqslant l$. Since (6.59) is identical in form with (6.15), we can use the results (6.29) and (6.31) and write directly

$$E'_n = \int \psi_n^{0*} \hat{H}' \psi_n^0 \, dz = H'_{nn} \tag{6.60}$$

$$a_k^{(n)} = \frac{1}{E_n^0 - E_k^0} \int \psi_k^{0*} \hat{H}' \psi_n^0 \, dz = \frac{H'_{kn}}{E_n^0 - E_k^0} \tag{6.61}$$

the normalization constant A^2 now being equal to unity. The new eigenfunctions ψ_n are still approximately normalized since the products of the coefficients $a_k^{(n)}$ can be neglected. Substituting from (6.37) and (6.58) we obtain for the correction to the eigenvalue of the nth state

$$\begin{aligned} E'_n &= \int \psi_n^{0*} \hat{H}' \psi_n^0 \, dz \\ &= -V_0 \frac{2}{l} \int_{z_1}^l \sin^2 \frac{n\pi}{l} z \, dz \\ &= -V_0 \frac{2}{n\pi} \frac{1}{2} \left(n\pi - \frac{n\pi}{l} z_1 + \frac{1}{2} \sin \frac{2n\pi}{l} z_1 \right) \\ &= -V_0 \left(\frac{\delta}{l} - \frac{1}{2n\pi} \sin \frac{2n\pi}{l} \delta \right) \end{aligned} \tag{6.62}$$

For small values of the argument $2n\pi\delta/l$ this becomes approximately equal to

$$E'_n \approx -V_0 \frac{2}{3} \pi^2 n^2 \frac{\delta^3}{l^3} \tag{6.63}$$

which is exactly the same as (6.54). However, using the general perturbation method, we can now also write an expression for the coefficients of the Fourier expansion of the correction functions ψ'_n, the new, perturbed eigenfunctions of the system being $\psi_n = \psi_n^0 + \psi'_n$. Substituting in (6.61) we find that

$$\begin{aligned} a_k^{(n)}(E_k^0 - E_n^0) &= -\int \psi_k^{0*} \hat{H}' \psi_n^0 \, dz \\ &= V_0 \frac{2}{l} \int_{z_1}^l \sin \frac{k\pi}{l} z \sin \frac{n\pi}{l} z \, dz \\ &= V_0 \frac{2}{l} \frac{1}{2} \left\{ \frac{\sin(k+n)\pi z_1/l}{(k+n)\pi/l} - \frac{\sin(k-n)\pi z_1/l}{(k-n)\pi/l} \right\} \\ &= (-1)^{k+n} V_0 \left\{ \frac{\sin(k-n)\pi\delta/l}{(k-n)\pi} - \frac{\sin(k+n)\pi\delta/l}{(k+n)\pi} \right\} \end{aligned} \tag{6.64}$$

Since $E_n^0 = n^2 E_1^0$ and $E_k^0 = k^2 E_1^0$ we can simplify (6.64) for small values of the argument

$$a_k^{(n)} \approx (-1)^{k+n} \frac{V_0}{E_1} \frac{2kn}{k^2 - n^2} \frac{1}{3} \pi^2 \frac{\delta^3}{l^3} \tag{6.65}$$

Let us now briefly recapitulate the technique of perturbation calculations as used in this chapter. Bearing in mind the basic linearity of the eigenvalue equations of the type (6.15) or, in particular, (6.59), we assume that the operator can be split into two parts: the first, referring to a known or unperturbed system, and the second, referring to those characteristics of the new, or perturbed system, which make it different from the old. Assuming that the perturbation is relatively small, an important condition for real success in the calculations, we obtain integrals of the form O'_{kn} or H'_{kn}; this gives us directly the correction terms to the eigenvalues and eigenfunctions of the old system, which are required to convert them to the eigenvalues and eigenfunctions of the new or perturbed system. In principle, the method is quite general and straightforward but the corresponding expressions may become quite involved especially if higher order corrections, which were not discussed in this chapter, are also required.[7] Since, however, in practice, most such calculations would now be carried out on a fast digital computer, it is only necessary for a non-specialist to understand the principles involved.

6.6. Perturbation of degenerate systems

So far we have carefully avoided any mention of degeneracy, although the validity of both (6.29) and (6.31) depends on the condition that *all* eigenvalues E_n are different. Since, in practice, we are most likely to deal with three-dimensional systems and since such systems usually conceal numerous degeneracies, as was pointed out in section 5.1, we must obviously amend our perturbation technique to allow for this. Fortunately this can be done, although the algebraic complications grow rapidly as the order of degeneracy increases. However, it will suffice for our purpose of illustration to consider the simplest case of a two-fold degeneracy only, two eigenstates, say m and n, having the same energy eigenvalue $E_m = E_n$.

Consider first the question of the orthogonality of the associated eigenfunctions. We can see from (5.2) that if $E_m = E_n$ the integral on the right-hand side of the equation no longer has to be zero when $m \neq n$, so that the corresponding eigenfunctions ψ_m and ψ_n may now be non-orthogonal. However, since the Schrödinger equation is linear, we can form two independent linear combinations of ψ_m and ψ_n, say

$$\psi_c(\mathbf{r}) = a_m^{(c)} \psi_m(\mathbf{r}) + a_n^{(c)} \psi_n(\mathbf{r}) \tag{6.66}$$

$$\psi_d(\mathbf{r}) = a_m^{(d)} \psi_m(\mathbf{r}) + a_n^{(d)} \psi_n(\mathbf{r}) \tag{6.67}$$

and impose the condition that they be orthogonal so that

$$\int \psi_d^* \psi_c \, d\mathbf{r} = 0 \tag{6.68}$$

Since, furthermore, ψ_c and ψ_d must be normalized (see (5.6)), this, together with (6.68) imposes three different conditions on the four constants, indicating not only that (6.66), (6.67) are always possible, but also that in fact there is an infinite number of ways in which the functions can be arranged. We can therefore assume that although the original eigenfunctions ψ_m and ψ_n may not necessarily be orthogonal, they can always be transformed with the help of (6.66), (6.67) into a pair of eigenfunctions ψ_c and ψ_d which are. Henceforth we will assume that, in considering perturbations, we only have to deal with orthogonal eigenfunctions, irrespective of whether they do or do not belong to degenerate eigenstates.

Having disposed of the problem of non-orthogonality which may be associated with degeneracy, we can now consider the perturbation method itself, assuming, for simplicity, only a two-fold degeneracy of the energy levels m and n. Since now the eigenfunctions ψ_m and ψ_n cannot be used directly in our perturbation calculations, we will consider a composite eigenfunction of the form

$$\psi_{mn}^0 = b_m \psi_m^0 + b_n \psi_n^0 \tag{6.69}$$

where zero superscripts again indicate the eigenfunctions of the original, unperturbed system. For ψ_{mn}^0 to be normalized (see (5.6))

$$b_m^* b_m + b_n^* b_n = 1 \tag{6.70}$$

Bearing in mind (6.56) let us now substitute $\psi_{mn} = \psi_{mn}^0 + \psi_{mn}'$ in the general eigenvalue equation of the last section (see (6.59)). Retaining first order terms only, we obtain

$$\hat{H}^0 \psi_{mn}^0 + \hat{H}^0 \psi_{mn}' + \hat{H}' \psi_{mn}^0 = E^0 \psi_{mn}^0 + E^0 \psi_{mn}' + E' \psi_{mn}^0 \tag{6.71}$$

But since ψ_m^0 and ψ_n^0 and thus ψ_{mn}^0 are the eigenfunctions belonging to the unperturbed operator $\hat{H}^0$, the first terms on both sides of (6.71) cancel. Rearranging the terms and substituting from (6.69) we now obtain

$$(\hat{H}^0 - E^0)\psi_{mn}' = b_m(E' - \hat{H}')\psi_m^0 + b_n(E' - \hat{H}')\psi_n^0 \tag{6.72}$$

Let us now express the correction function ψ_{mn}' as an infinite series in terms of the original eigenfunctions of the unperturbed system ψ_i^0, just as we have done in (6.24). This is always possible because ψ_i^0 form a complete set and are assumed to be orthogonal, following (6.66), (6.67). This gives

$$\psi_{mn}' = \sum_i a_i^{(mn)} \psi_i^0 \tag{6.73}$$

Substituting (6.73) in (6.72) we obtain

$$\sum_i a_i^{(mn)}(E_i^0 - E^0)\psi_i^0 = E_m'(b_m\psi_m^0 + b_n\psi_n^0) - \hat{H}'b_m\psi_m^0 - \hat{H}'b_n\psi_n^0 \quad (6.74)$$

Multiply (6.74) by ψ_m^{0*} on the left and integrate it with respect to z between $-\infty$ and $+\infty$. In view of the orthogonality property of ψ_i^0 we obtain, since $E_m^0 = E_n^0 = E^0$,

$$0 = b_m E_m' - b_m H_{mm}' - b_n H_{mn}' \quad (6.75)$$

where H_{ij}' are defined by (6.61). Similarly, multiplying (6.74) by ψ_n^{0*} and integrating we obtain

$$0 = b_n E_n' - b_m H_{nm}' - b_n H_{nn}' \quad (6.76)$$

For all other eigenfunctions we obtain, multiplying (6.74) by ψ_k^0 and integrating

$$(E_k^0 - E^0)a_k^{(mn)} = -b_m H_{km}' - b_n H_{kn}' \quad (6.77)$$

Expressions (6.75) and (6.76) form a set of homogeneous algebraic equations in b_m, b_n; they have a non-trivial solution only when the determinant

$$\begin{vmatrix} H_{mm}' - E' & H_{mn}' \\ H_{nm}' & H_{nn}' - E' \end{vmatrix} = 0 \qquad [6.78]$$

i.e., when

$$(H_{mm}' - E')(H_{nn}' - E') - H_{mn}' H_{nm}' = 0 \quad (6.78)$$

Equation (6.78), which is often called the 'secular equation', has two roots E_m' and E_n' which are the two corrections to the common energy eigenvalues $E^0 = E_m^0 = E_n^0$ of the unperturbed system. If the roots are different the perturbation removes the degeneracy and the two energy eigenvalues of the perturbed system are now given by

$$E_m = E^0 + E_m'$$
$$E_n = E^0 + E_n' \qquad (6.79)$$

This is a very common situation in quantum mechanics. Since the degeneracy is often the result of some geometrical symmetry of the system, a perturbation may well destroy this symmetry and thus remove the degeneracy. On the other hand, if the two roots of the secular equation (6.78) are equal the new eigenvalues E_m and E_n still remain the same; in physical terms this means that the perturbation preserves the symmetry of the system and does not remove the degeneracy. The splitting of energy levels due to orbital-spin magnetic moment interactions or Zeeman splitting due to the presence of a magnetic field, both

discussed in chapter 4, are excellent examples of the removal of degeneracy by reducing the symmetry of a system.

Substituting E'_m and E'_n back in (6.75), (6.76) gives two different coefficient ratios $b_m^{(m)}/b_n^{(m)}$ and $b_m^{(n)}/b_n^{(n)}$; this, together with the normalization condition (6.70), defines the magnitude (though not the phase) of the coefficients: $b_m^{(m)}$, $b_n^{(m)}$ from the correction term E'_m and $b_m^{(n)}$, $b_n^{(n)}$ from the correction term E'_n. Rearranging (6.77) we now obtain an expression for the general coefficient $a_k^{(mn)}$ of the series expansion (6.73) for the correction function ψ'_{mn}

$$a_k^{(mn)} = \frac{b_m H'_{km} + b_n H'_{kn}}{E^0 - E_k^0} \tag{6.80}$$

However, since now we have two sets of coefficients, one corresponding to E'_m and the other to E'_n, it is more appropriate to write

$$a_k^{(m)} = \frac{b_m^{(m)} H'_{km} + b_n^{(m)} H'_{kn}}{E^0 - E_k^0} \tag{6.80m}$$

$$a_k^{(n)} = \frac{b_m^{(n)} H'_{km} + b_n^{(n)} H'_{kn}}{E^0 - E_k^0} \tag{6.80n}$$

This expression is valid for all k except $k=m$ and $k=n$, but then, to the first order of approximation, no correction term is required for either ψ_m^0 or ψ_n^0, so that the complete new eigenfunctions of the perturbed system are given by

$$\psi_m = b_m^{(m)} \psi_m^0 + b_n^{(m)} \psi_n^0 + \sum_i a_i^{(m)} \psi_i^0 \tag{6.81m}$$

$$\psi_n = b_m^{(n)} \psi_m^0 + b_n^{(n)} \psi_n^0 + \sum_i a_i^{(n)} \psi_i^0 \tag{6.81n}$$

where $i \neq m, n$. Here ψ_m and ψ_n are the new eigenfunctions of the perturbed state and respectively correspond to the new eigenvalues E_m and E_n defined by (6.79).

It should be added that although all a_i coefficients tend to zero as $\hat{H}' \to 0$, this does not apply to the four coefficients b; we find from the secular equation (6.78) that their ratios depend on the algebraic form of the perturbation operator $\hat{H}'$ and not on its magnitude. Thus, the two zero order wave functions

$$\psi_{mn}^{0(m)} = b_m^{(m)} \psi_m^0 + b_n^{(m)} \psi_n^0 \tag{6.82m}$$

$$\psi_{mn}^{0(n)} = b_m^{(n)} \psi_m^0 + b_n^{(n)} \psi_n^0 \tag{6.82n}$$

play a special role being characteristic of the algebraic form of the perturbation operator $\hat{H}'$. This unique property of such eigenfunctions will be used in the discussion of identical particles, as we shall see in chapter 8.

Problems

1. Consider the problem of a bound particle in classical mechanics and explain why the same problem is mathematically much more complex in quantum mechanics.

2. Express V_0, I_0 in terms of $V(z)$, $I(z)$. We shall need this in chapter 10.

3. Equation (6.2) applies to an idealized transmission line. Is it still valid without restriction when the transmission line is built from a large number of identical T or Π sections connected in tandem? If the number of such sections is N, could we have a mode for which $n > N$? If not, why not?

4. Can you suggest why condition (6.7) has been introduced although it is not required in electrical engineering and makes the problem less general?

5. Discuss in some detail the physical consequences of the requirement that the slope of either I or V should be continuous across the junction $1-1'$ in Fig. 6.2. Use transmission line equations.

6. Calculate one or two points in Fig. 6.3 using the transcendental equation (6.8).

7. Derive an equivalent of (6.13) by retaining one higher order term in (6.11). What does this tell you about the accuracy of (6.13)?

8. Discuss the meaning of an 'operator' in connection with our transmission line model. Can you suggest any basic differences between operators as used, for example, in electrical engineering and quantum mechanics? Consider the general eigenvalue equation, (3.63).

9. Derive (6.27) from (6.21) avoiding the use of the summation sign. Do the same in deriving (6.29) and (6.31) from (6.28). Can you see why $\hat{O}I$ is again different from $I\hat{O}$?

10. Derive (6.35) expressing $\sin x$ as an infinite series.

11. Explain what happens when the point $1-1'$ of Fig. 6.2 coincides with one of the nodes. How many modes will be affected by this situation?

12. Using the procedure suggested in the text eliminate the integration constants from (6.42) and (6.43) and derive (6.49).

13. Derive an equivalent of (6.54) by retaining one more term in (6.53). What is the relative accuracy of (6.54) as n increases?

14. Compare (6.58) and (6.19). Discuss similarities and differences. Have we gained anything by using a transmission line model first? Discuss Fig. 6.6.

15. What would happen in (6.28) if the eigenvalues of two different modes were identical? (This situation cannot occur in one-dimensional systems for physical reasons, but is quite common in three-dimensional situations as we have already seen.) Consult (5.2).

16. Substitute (6.69) in (6.71) and derive (6.72), making use of the properties of ψ_{mn}^0.

17. Derive (6.75)–(6.77) avoiding the use of the summation sign in (6.74).

18. Obtain (6.80m) and (6.80n) from (6.77) by substituting in it the roots of the determinantal equation (6.78).

19. Discuss the physical significance of (6.82 m and n).

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7. Time-dependent Perturbations, Matrices

So far we have considered the so-called time-independent perturbations, i.e., the calculation of eigenvalues and eigenfunctions of one stationary state in terms of similar quantities of another, usually simpler, stationary state, the two states differing slightly in the values of their parameters. Since stationary states can only be observed indirectly, the above procedure has its limitations. What we would now like to do is to develop an approximate method which would enable us to calculate how a given system evolves in time under the influence of a perturbing force and not merely tell us what its final state is likely to be. In terms of electrical engineering, this is frequently equivalent to the analysis of transients caused by small changes in the value of the parameters of the system, such changes commonly being in the form of step functions, pulses, or truncated sine waves. In quantum mechanics, time-dependent perturbations tell us how a system interacts with its environment; thus, in the case of line spectra, the individual lines observed represent the transitions between different stationary states, whose properties can only be deduced rather than observed.

7.1. General approach

In chapter 6 we have found that the most general and, at the same time, probably the most convenient representation of the correction function ψ'_n is in terms of the eigenfunctions of the unperturbed system ψ^0_n. Furthermore, we were able to show in section 5.5 that for conservative systems the coefficients a_n of a more general expansion involving $\Psi^0_n(z, t)$ are independent of time even though the functions $\Psi^0_n(z, t)$ vary with time in a periodic manner. We are going to use the same series representation in this chapter except that now the coefficients of the expansion are expected to vary with time.

We know from (3.60a), (3.61), and (5.36) that the time-dependent Schrödinger equation can be written as

$$\hat{H}\Psi = j\hbar \frac{\partial \Psi}{\partial t} \tag{7.1}$$

where, for non-conservative systems, the Hamiltonian operator $\hat{H}$ is

normally a function of time. Let us assume that, following (6.56),

$$\hat{H} = \hat{H}^0 + \hat{H}' \tag{7.2}$$

where only the perturbation part of the operator, $\hat{H}'$, is time dependent, the perturbation being applied to a stationary system characterized by a time-independent operator $\hat{H}^0$ and the corresponding energy eigenvalues E^0 and eigenfunctions $\Psi^0(z, t)$.

Following the example of (5.34), let us now assume that the wave functions of the perturbed system can be expressed in the form of an infinite series

$$\Psi(z, t) = \sum_i a_i(t)\Psi_i^0(z, t) \tag{7.3}$$

where

$$\Psi_i^0(z, t) = \psi_i^0(z)\, e^{-jE_i^0 t/\hbar} \tag{7.4}$$

satisfy

$$\hat{H}^0\Psi = j\hbar\, \frac{\partial\Psi}{\partial t} = E^0\Psi \tag{7.5}$$

i.e., are the eigenfunctions of the unperturbed operator $\hat{H}^0$. In (7.3) the possible time dependence of the coefficients of expansion $a_i(t)$ has been indicated explicitly. Substituting (7.3) in (7.1) we now obtain, in view of (7.2)

$$\sum_i a_i(t)\hat{H}^0\Psi_i^0 + \sum_i a_i(t)\hat{H}'\Psi_i^0 = j\hbar \sum_i \dot{a}_i(t)\Psi_i^0 + j\hbar \sum_i a_i(t)\frac{\partial\Psi_i^0}{\partial t} \tag{7.6}$$

But, from (7.5), the first and last series of (7.6) cancel out term by term. Multiplying the rest of (7.6) by $\Psi_k^0{}^*$ and integrating with respect to z, assuming for simplicity that the system is one-dimensional, we obtain

$$j\hbar\dot{a}_k(t) = \sum_i a_i(t)\int \Psi_k^0{}^*\hat{H}'\Psi_i^0\, dz$$
$$= \sum_i a_i(t)\overline{H}'_{ki} \tag{7.7}$$

remembering that Ψ_i^0 are orthogonal. (The bar over $\overline{H}'$ indicates that we operate on Ψ and not on ψ.) This equation can be conveniently rewritten using matrix notation

$$j\hbar \begin{bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} \overline{H}'_{11} & \overline{H}'_{12} & \overline{H}'_{13} & \cdots \\ \overline{H}'_{21} & \overline{H}'_{22} & \overline{H}'_{23} & \cdots \\ \overline{H}'_{31} & \overline{H}'_{32} & \overline{H}'_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \tag{7.7}$$

Naturally, if the operator $\hat{H}$ is time independent we have $\hat{H}' = 0$ and from [7.7] all $\dot{a}_1 = 0$, the coefficients of expansion a_i now being constant in time, as shown in section 5.5. Both (7.7) and [7.7] are deceptively simple, although, in principle, they fully describe the way in which all the coefficients of expansion $a_k(t)$ evolve in time under the influence of the time-dependent perturbation operator $\hat{H}'$.

As a rule, the fundamental equation [7.7] is too difficult to solve and we have to assume that the effect of the perturbation $\hat{H}'$ is so small that all the cross-product terms involving primed quantities can be neglected, a procedure we have already adopted in the discussion of the time-independent perturbations described in the previous chapter. Put

$$a_i(t) = a_i^0 + a_i'(t) \tag{7.8}$$

where $a_i^0 = a_i^0(t_0)$ are the coefficients of expansion of the wave function $\Psi(z, t)$ at the time $t = t_0$, i.e., just before the perturbation is actually applied; these coefficients are assumed to be known, if necessary from calculations of the type described in section 5.5. Substituting (7.8) in (7.7) and leaving the first order terms in primed quantities only, we obtain

$$j\hbar(\dot{a}_k^0 + \dot{a}_k') = (a_1^0 + a_1')\overline{H}_{k1}' + (a_2^0 + a_2')\overline{H}_{k2}' + \cdots$$
$$= a_1^0\overline{H}_{k1}' + a_2^0\overline{H}_{k2}' + \cdots$$
$$= \sum_i a_i^0 \overline{H}_{ki}' \tag{7.9}$$

But, by definition, a_i^0 are independent of time, so that $\dot{a}_k^0 = 0$, and (7.9) reduces to the following expression, which again can be written in matrix notation

$$j\hbar \begin{bmatrix} \dot{a}_1' \\ \dot{a}_2' \\ \dot{a}_3' \\ \vdots \end{bmatrix} = \begin{bmatrix} \overline{H}_{11}' & \overline{H}_{12}' & \overline{H}_{13}' & \cdots \\ \overline{H}_{21}' & \overline{H}_{22}' & \overline{H}_{23}' & \cdots \\ \overline{H}_{31}' & \overline{H}_{32}' & \overline{H}_{33}' & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} a_1^0 \\ a_2^0 \\ a_3^0 \\ \vdots \end{bmatrix} \tag{7.10}$$

Equations [7.10], which are approximate, form the basis of our future calculations in this chapter. As in the case of [6.36] they show that a perturbation, whether time dependent or time independent, invariably introduces 'mode mixing', in the parlance of electrical engineering; the value of the time-dependent off-diagonal terms expresses the degree of coupling between different eigenstates which is introduced by the perturbation. Clearly, the rate of change of each coefficient a_i' depends among other things on the matrix elements $\overline{H}_{ki}'$ which 'connect' different stationary (pure) states. The calculation of the terms containing $\overline{H}_{ki}'$ forms the central task in the solution of most practical problems concerning the time-dependent behaviour of quantum mechanical systems.

For example, the selection rules which appear in the theory of spectra largely depend on the properties of the off-diagonal terms, the probability of a transition generally depending on the magnitude of the corresponding $\overline{H}'_{ki}$ term.

7.2. Step function perturbation

The simplest possible time-dependent perturbation is that described by a step function. If the system is initially in an eigenstate m, then $a_i^0 = 1$ for $i = m$ and $a_i^0 = 0$ for all $i \neq m$; [7.10] then reduces to

$$
j\hbar
\begin{bmatrix}
\vdots \\
\dot{a}'_k \\
\dot{a}'_m \\
\dot{a}'_n \\
\vdots
\end{bmatrix}
=
\begin{bmatrix}
& \vdots & \vdots & \vdots & \\
\cdots & \overline{H}'_{kk} & \overline{H}'_{km} & \overline{H}'_{kn} & \cdots \\
\cdots & \overline{H}'_{mk} & \overline{H}'_{mn} & \overline{H}'_{mn} & \cdots \\
\cdots & \overline{H}'_{nk} & \overline{H}'_{nm} & \overline{H}'_{nn} & \cdots \\
& \vdots & \vdots & \vdots &
\end{bmatrix}
\begin{bmatrix}
\vdots \\
0 \\
1 \\
0 \\
\vdots
\end{bmatrix}
\qquad [7.11]
$$

For a typical line of [7.11] we obtain

$$
\begin{aligned}
j\hbar\dot{a}'_k &= \overline{H}'_{km} \\
&= \int \Psi_k^{0*} \hat{H}' \Psi_m^0 \, dz \\
&= \int \psi_k^{0*} \, e^{jE_k^0 t/\hbar} \hat{H}' \psi_m^0 \, e^{-jE_m^0 t/\hbar} \, dz \\
&= e^{j(E_k^0 - E_m^0)t/\hbar} \int \psi_m^{0*} \hat{H}' \psi_m^0 \, dz \\
&= H'_{km} \, e^{j(E_k^0 - E_m^0)t/\hbar} \\
&= H'_{km} \, e^{j\omega_{km}t}
\end{aligned}
\qquad (7.12)
$$

where the 'beat' angular frequency

$$
\omega_{km} = (E_k^0 - E_m^0)/\hbar
\qquad (7.13)
$$

Since, in the case of a step function, $\hat{H}'$ does not depend on time after $t = 0$, H'_{km} is also time independent and we can integrate (7.12) directly, so that

$$
a'_k(t) = -\frac{H'_{km}}{\hbar} \frac{\exp(j\omega_{km}t) - 1}{\omega_{km}}
\qquad (7.14)
$$

where, by definition, $a'_k = 0$ at $t = 0$. Thus, a sudden perturbation applied to a system which is in an eigenstate m, momentarily excites all the other states, making it appear that the system is in a composite state in terms of the original wave functions Ψ_k^0. This behaviour is quite familiar from

acoustics or electrical engineering, where a step excitation of a resonator tends to excite all the other modes. It should be noted that (7.14) cannot be used when $k=m$; this is simply due to the fact that, to the first approximation the perturbation does not affect the amplitude a_m, which remains equal to a_m^0, giving $a_m'=0$ by definition. (In normalizing, all primed terms appear as squares $|a_k'|^2$ and must thus be neglected in comparison with $|a_m^0|^2=1$.)

By squaring both sides of (7.14) we find that the probability of finding the system in state k at time t, or the frequency of occurrence of the energy eigenvalue E_k, as discussed in section 5.3 is given by

$$a_k'^* a_k' = \frac{H_{km}'^* H_{km}'}{\hbar^2} \left\{ \frac{\sin \frac{1}{2}\omega_{km} t}{\frac{1}{2}\omega_{km}} \right\}^2 \tag{7.15}$$

The expression in brackets is plotted in Fig. 7.1 as a function of ω_{km}. For $\omega_{km} \to 0$ the function becomes equal to t^2, which is the rate at which its peak grows with time. Since the width of the main lobe decreases with t and its height increases as t^2, the corresponding area is proportional to t;
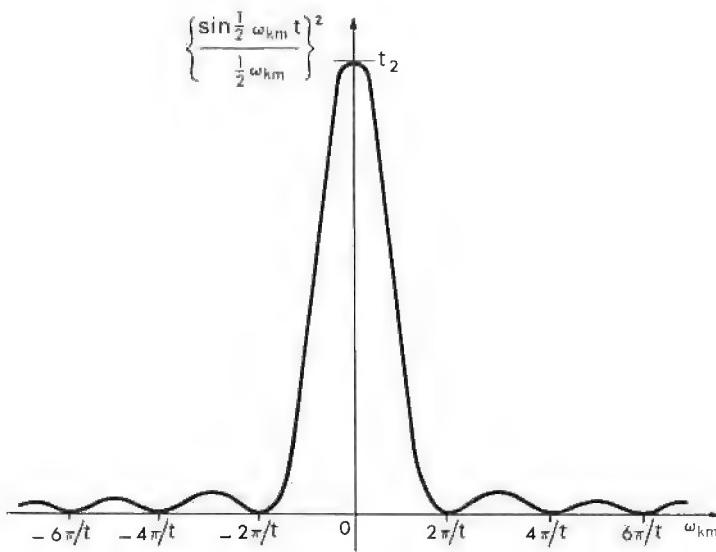
Fig. 7.1. The ω_{km}-dependent part of the probability density function $a_k'^* a_k'$ given by (7.15).

thus, for small perturbations, the probability that $k=m$, for which $\omega_{km}=0$, remains the most powerfully excited state, grows with time. The same applies to other states contained within the main lobe of the curve.

7.3. Harmonic perturbation

Let us now assume that the perturbation operator $\hat{H}'$, is a step function modulated by a pure sine wave of angular frequency ω_0, so that

$$\hat{H}'(z, t) = A(z) \sin \omega_0 t \tag{7.16}$$

for $t > 0$ and zero for $t < 0$. Equations [7.10] again become

$$j\hbar \begin{bmatrix} \vdots \\ \dot{a}'_k \\ \dot{a}'_m \\ \dot{a}'_n \\ \vdots \end{bmatrix} = \begin{bmatrix} & \vdots & \vdots & \vdots & \\ \cdots & \bar{H}'_{kk} & \bar{H}'_{km} & \bar{H}'_{kn} & \cdots \\ \cdots & \bar{H}'_{mk} & \bar{H}'_{mm} & \bar{H}'_{mn} & \cdots \\ \cdots & \bar{H}'_{nk} & \bar{H}'_{nm} & \bar{H}'_{nn} & \cdots \\ & \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix} \tag{7.17}$$

which is superficially similar to [7.11]. Writing a typical line of [7.17] we now obtain, however,

$$j\hbar \dot{a}'_k = \bar{H}'_{km}$$

$$= \int \Psi_k^{0*} \hat{H}' \Psi_m^0 \, dz$$

$$= \int \psi_k^{0*} \, e^{jE_k^0 t/\hbar} A(z) \sin \omega_0 t \psi_m^0 \, e^{-jE_m^0 t/\hbar} \, dz$$

$$= e^{j\omega_{km} t} \sin \omega_0 t \int \psi_k^{0*} A(z) \psi_m^0 \, dz$$

$$= H'_{km}(z) \, e^{j\omega_{km} t} \sin \omega_0 t \tag{7.18}$$

Expressing $\sin \omega_0 t$ in terms of the exponential functions, we can integrate (7.18) with respect to time, obtaining

$$a'_k(t) = \frac{jH'_{km}}{2\hbar} \left\{ \frac{\exp j(\omega_{km} + \omega_0)t - 1}{\omega_{km} + \omega_0} - \frac{\exp j(\omega_{km} - \omega_0)t - 1}{\omega_{km} - \omega_0} \right\} \tag{7.19}$$

This equation clearly shows that any states with energies

$$E_i^0 = E_m^0 - \hbar\omega_0$$
$$E_i^0 = E_m^0 + \hbar\omega_0 \tag{7.20}$$

will be strongly affected by the perturbation. The probability density function $a'^*_k a'_k$ corresponding to (7.19) is rather complicated, but near the two 'resonances' E_i^0 given by (7.20) it looks very much like the curve of Fig. 7.1, but with a factor $\frac{1}{4}$ in front and the origin shifted either to $-\omega_0$ or $+\omega_0$.

This type of time-dependent perturbation is very important, since it is

used for the so-called semiclassical discussion of interaction between electromagnetic radiation and matter[1, 2, 3] where the electromagnetic field is treated classically and the energy quantization only applies to matter which is represented by harmonic oscillators. This problem is also of great importance in the theory of masers and lasers, where we are used to the idea that if electromagnetic radiation of frequency ω_0 is allowed to interact with matter, the atoms are very likely to be 'pumped' from the ground state to an excited state, differing in energy by $\hbar\omega_0$; or, when amplification takes place, the atoms are likely to drop from a higher to a lower energy state, the difference being equal to $\hbar\omega_0$. It is only with the help of time-dependent perturbation theory that these statements, often made in maser and laser work, can be substantiated.

7.4. Electric dipole transitions

Let us now consider an important example of the harmonic type of time-dependent perturbation in more detail and analyse the behaviour of a quantum mechanical harmonic oscillator subjected to the electric component of a sinusoidally varying electromagnetic field. We know from (3.60a) and (4.39) that the Hamiltonian operator of an unperturbed harmonic oscillator is given by

$$\hat{H}^0 = -\frac{\hbar^2}{2m_0}\frac{d^2}{dz^2} + \tfrac{1}{2}\kappa z^2 \tag{7.21}$$

where m_0 is used for the mass of the particle to distinguish it from the subscript m. We also know from (4.47) that a particle bound in a parabolic potential well can only assume energy states given by

$$E_m = (m + \tfrac{1}{2})\hbar\omega_c \tag{7.22}$$

where

$$\omega_c^2 = \frac{\kappa}{m_0} \tag{7.23}$$
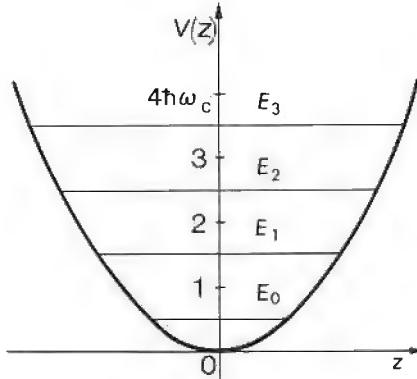
Fig. 7.2. Energy eigenvalues of a harmonic oscillator in units of $\hbar\omega_c$.

as shown in Fig. 7.2. If the particle has an electric charge, say $-e$, it can be subjected, in addition, to an electric force generated, for example, between the plates of a condenser, as shown in Fig. 7.3, or by a standing wave pattern. In the case of a condenser, the electric field **E** between the
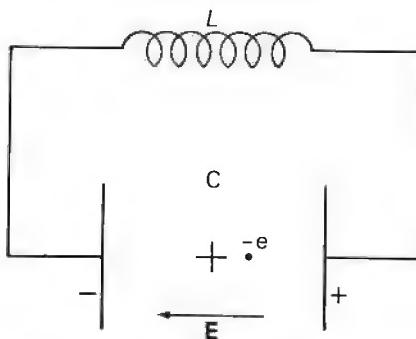
Fig. 7.3. An electron contained in a parabolic potential well (harmonic oscillator) and subjected to a perturbing electric field of frequency ω_c.

plates is constant in space and only varies (sinusoidally) with time, so that the force on the particle of charge $-e$ is given by

$$F = -e\mathbf{E} \sin \omega_c t \tag{7.24}$$

Since, by definition, $F = -\partial V/\partial z$, where V is the potential, we obtain, integrating (7.24) with respect to z,

$$\hat{H}' = \hat{V}' = ez\mathbf{E} \sin \omega_c t \tag{7.25}$$

where $\hat{H}'$ is the perturbing part of the Hamiltonian operator and ez has the appearance of an electric dipole generated by two charges, $-e$ and $+e$ which are distance z apart. Consequently, transitions due to the perturbation operator of this form are often referred to in spectroscopy as 'electric dipole transitions'. Using (7.18), (7.19) and knowing the eigenfunctions of the harmonic oscillator, given by (4.45) and (4.46), we can now calculate explicitly the important matrix elements H'_{km}.

Let us assume, for simplicity, that the harmonic oscillator is in its ground state, $m=0$. Then

$$H'_{10} = e\mathbf{E} \int \psi_1^{0*} z \psi_0^0 \, dz$$

$$= \frac{e\mathbf{E}}{\alpha} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int \zeta^2 \, e^{-\zeta^2} \, d\zeta$$

$$= \frac{e\mathbf{E}}{\alpha} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{\pi^{\frac{1}{2}}}{2}$$

$$= \frac{1}{\sqrt{2}} \frac{e\mathbf{E}}{\alpha} \tag{7.26}$$

$$H'_{20} = e\mathsf{E} \int \psi_2^{0*} z \psi_0^0 \, dz$$

$$= \frac{e\mathsf{E}}{\alpha(2\pi)^{\frac{1}{2}}} \int \zeta(\zeta^2 - 1) \, e^{-\zeta^2} \, d\zeta$$

$$= 0 \tag{7.27}$$

$$H'_{30} = e\mathsf{E} \int \psi_3^{0*} z \psi_0^0 \, dz$$

$$= \frac{e\mathsf{E}}{\alpha(3\pi)^{\frac{1}{2}}} \int \zeta^2 (2\zeta^2 - 3) \, e^{-\zeta^2} \, d\zeta$$

$$= \frac{e\mathsf{E}}{\alpha(3\pi)^{\frac{1}{2}}} \left\{ 2 \cdot \frac{6}{8} \pi^{\frac{1}{2}} - 3 \cdot \frac{2}{4} \pi^{\frac{1}{2}} \right\}$$

$$= 0 \tag{7.28}$$

Due to the algebraic properties of Hermite polynomials, all the higher off-diagonal terms H'_{k0} are zero. Thus, the only possible transition from the ground level is that to level 1, all the other transitions being forbidden, as long as the potential well is exactly parabolic (in practice, this is hardly ever the case, and the other transitions are not completely absent, but merely rare, the corresponding spectral lines being very weak). In general, it is possible to show[4] that if a harmonic oscillator is originally in an eigenstate m, the only allowed upward transition is that to an energy level n, where $n = m + 1$, the corresponding off-diagonal term being equal to

$$H'_{nm} = \left(\frac{n}{2} \right)^{\frac{1}{2}} \frac{e\mathsf{E}}{\alpha} \tag{7.29}$$

Similarly, we can show that the downward transitions are also severely limited in number. Since the integrals (7.26)–(7.28) are quite symmetrical, we can see that $H'_{01} \neq 0$ so that this transition is permitted, but H'_{02} and H'_{03} are both zero, no corresponding transitions being allowed. If the particle is in the energy state $m = 2$, we find that

$$H'_{12} = e\mathsf{E} \int \psi_1^{0*} z \psi_2^0 \, dz$$

$$= \frac{e\mathsf{E}}{\alpha\pi^{\frac{1}{2}}} \int \zeta^2 (2\zeta^2 - 1) \, e^{-\zeta^2} \, d\zeta$$

$$= \frac{e\mathsf{E}}{\alpha} \tag{7.30}$$

or, in general,[4] for a downward transition from a state m to a state

$k = m - 1$, we obtain

$$H'_{km} = \left(\frac{m}{2}\right)^{\frac{1}{2}} \frac{e\mathsf{E}}{\alpha} \qquad (7.31)$$

all other transitions being forbidden.

The simple example of a harmonic oscillator shows very clearly that in considering the suitability of materials for quantum-electronic applications, e.g., masers or lasers, it is not enough to consider the available energy levels and to provide electromagnetic radiation of suitable frequency ω which is just right to match a given energy gap $\hbar\omega$—it is also necessary to ensure that the corresponding transitions are allowed, i.e., that the appropriate off-diagonal terms H'_{ij} are not equal to zero and that they are sufficiently probable to be of practical interest. A considerable amount of labour is usually required to obtain this information, as is clearly shown elsewhere.[5]

When an atom has a magnetic dipole,[6, 7] for example, when its azimuthal quantum number $l \neq 0$, it can also respond to the magnetic component of the electromagnetic field, although the corresponding H'_{ij} terms are usually smaller than corresponding electric dipole transitions by a factor of 10^4. However, sometimes due to the different algebraic form of H'_{ij} in the two cases, the transitions which are forbidden in the electric case may be allowed in the magnetic case, although then very strong magnetic fields are required to make up for the smallness of H'_{ij}.

It is of interest to note that in the case of two resonant circuits which are lightly coupled, the stored energy continuously oscillates between the two circuits. The same applies to the probability of transition in the case of a two-level atomic system which can be analysed exactly.[8] This is in complete agreement with (7.19) where the t^2 growth of $a'_k{}^* a_k$ for $\omega_0 = \pm \omega_{km}$ merely indicates the first term in an expansion of the $\sin^2$ function valid for large a'_k. Finally, it should be added that, in some cases, the first order perturbation methods described in this chapter are inadequate and higher order perturbations have to be used. The reader is referred to other books on quantum mechanics for a further study of this topic.[9, 10]

7.5. Matrix mechanics

We have already noted that many quantum mechanical problems are particularly suitable for matrix representation. This is by no means a coincidence since matrices played a prominent role in the early development of quantum mechanics,[11] in an attempt to consider only those quantities which could actually be observed. In the case of atomic systems it was felt that frequency, intensity, and polarization of the emitted radiation were preferable to the concepts of position and velocity of an electron. This approach led to the development of the so-called

matrix mechanics which can be looked on as an alternative representation of quantum mechanics, as was suggested in chapter 1.

Since matrix notation is often used in parallel with wave representation, as we have done ourselves, it seems desirable to review very briefly some of the basic ideas of matrix mechanics, a more systematic presentation being available elsewhere[12]; this should also help us in placing [7.7], [7.10], and [6.36] in the wider context of a more general matrix representation.

Consider a complete set of one-dimensional, orthonormal functions $\zeta_i(z)$. Following the argument presented in section 5.5, we assume that such a set can be used for expanding an arbitrary wave function $\Psi(z, t)$, so that

$$\Psi(z, t) = \sum_i a_i(t)\zeta_i(z) \tag{7.32}$$

where $i \to \infty$. By analogy with the three-dimensional vectors,

$$\mathbf{A} = \sum_i a_i\mathbf{X}_i \tag{7.33}$$

where $i = 1, 2, 3$ and $\mathbf{X}_i$ are three orthogonal unit vectors, we refer to the orthonormal set of ζ_i functions as the coordinates or coordinate vectors spanning an infinite-dimensional function or vector space; the coefficients a_i are then called the components of the arbitrary function or vector $\Psi(z, t)$. Since in quantum mechanics $\Psi(z, t)$ and ζ_i are in general complex, the corresponding vector space is called a Hilbert space. We can now express $\Psi(z, t)$ in terms of its components alone by forming a column matrix

$$\Psi = [a_i] = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \tag{7.34}$$

just as it is usual to write for an ordinary vector $\mathbf{u} = (u_1, u_2, u_3)$. Equation [7.34] is called the matrix representation of Ψ to the basis ζ_i.

Substituting from (7.32) we now obtain the following expression for the normalization condition of a wave function

$$
\begin{aligned}
1 = \int \Psi^*\Psi \, dz &= \int \sum_j \sum_i a_j^* a_i \zeta_j^* \zeta_i \, dz \\
&= \sum_j \sum_i a_j^* a_i \, \delta_{ij} \\
&= \sum_i a_i^* a_i \tag{7.35}
\end{aligned}
$$

or

$$1 = [a_i]^\dagger [a_i] = [a_1^*, a_2^*, a_3^*, \ldots] \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \qquad [7.35]$$

where, in general, $[a_{ij}]^\dagger$ is called the adjoint or Hermitian adjoint of $[a_{ij}]$ and is formed by first transposing $[a_{ij}]$ and then making all its terms complex conjugate, so that $[a_{ij}]^\dagger = [a_{ji}^*]$. It is instructive to compare (7.35) with (5.7) and problem 6 of chapter 5.

Similarly, the orthogonality condition of two wave functions Ψ_α and Ψ_β can now be expressed in the form

$$\begin{aligned} 0 = \int \Psi_\beta^* \Psi_\alpha \, dz &= \int \sum_j \sum_i a_{\beta j}^* a_{\alpha i} \zeta_j^* \zeta_i \, dz \\ &= \sum_j \sum_i a_{\beta j}^* a_{\alpha i} \, \delta_{ij} \\ &= \sum_i a_{\beta i}^* a_{\alpha i} \end{aligned} \qquad (7.36)$$

or

$$0 = [a_{\beta i}]^\dagger [a_{\alpha i}] = [a_{\beta 1}^*, a_{\beta 2}^*, a_{\beta 3}^*, \ldots] \begin{bmatrix} a_{\alpha 1} \\ a_{\alpha 2} \\ a_{\alpha 3} \\ \vdots \end{bmatrix} \qquad [7.36]$$

Equation (7.36) looks exactly like an inner or scalar product of two three-dimensional vectors, $(\mathbf{u}, \mathbf{v}) = u_1 v_1 + u_2 v_2 + u_3 v_3$. Since such vectors are orthogonal when their scalar product is zero, by similarity functions satisfying (7.36) are also called orthogonal.

Let us now consider an operator $\hat{O}$ acting on an arbitrary wave function Ψ. Then, using (7.32) again, we obtain

$$\hat{O}\Psi = \hat{O} \sum_i a_i \zeta_i = \sum_i a_i \hat{O} \zeta_i = \sum_j \sum_i a_i \hat{O}_{ji} \zeta_j \qquad (7.37)$$

where in the last term we have expanded the new function $\hat{O}\zeta_i$ again in terms of the orthonormal set ζ_j, using a new symbol $\hat{O}_{ji}$ for the second set of coefficients of expansion. To find the coefficients $\hat{O}_{ji}$ we multiply as usual both sides of the series expansion of $\hat{O}\zeta_i$ by ζ_k^* and, integrating with respect to z, obtain

$$\int \zeta_k^* \hat{O} \zeta_i \, dz = \int \sum_j \zeta_k^* \hat{O}_{ji} \zeta_j \, dz = \hat{O}_{ki} \qquad (7.38)$$

Again by analogy with ordinary vector algebra, where $(\mathbf{u}, \mathbf{v}) = \sum_i u_i v_i$, the operation $\int g^*(z)f(z)\, dz = (g(z), f(z))$ is often called the inner product. Following [7.34] we now define, retaining the components of the new vector only,

$$\hat{O}\Psi = [\hat{O}_{ji}][a_i] = \begin{bmatrix} \hat{O}_{11} & \hat{O}_{12} & \hat{O}_{13} & \cdots \\ \hat{O}_{21} & \hat{O}_{22} & \hat{O}_{23} & \cdots \\ \hat{O}_{31} & \hat{O}_{32} & \hat{O}_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \qquad [7.37]$$

Thus in matrix notation an operator $\hat{O}$ is represented by an $i \times i$ matrix, $i \to \infty$, the elements of the matrix $\hat{O}_{ij}$ being given by (7.38). Equation [7.37] shows that, in general, the action of an operator in quantum mechanics can be represented by a transformation in Hilbert space of a corresponding n-dimensional vector $[a_i]$. Comparing (7.38) and (3.66a) we find that the individual terms of $[\hat{O}_{ij}]$ are closely related to the observables associated with the operator when the system is in an eigenstate or in transition between two eigenstates. On the other hand, from (3.66), in general the expectation or mean value of the operator is given by

$$\langle O \rangle = \int \Psi^* \hat{O} \Psi \, dz = \int \sum_j \sum_i a_j^* a_i \zeta_j^* \hat{O} \zeta_i \, dz$$
$$= \sum_j \sum_i a_j^* \hat{O}_{ji} a_i \qquad (7.39)$$

or

$$\langle O \rangle = [a_j]^\dagger [O_{ji}][a_i]$$

$$= [a_1^*, a_2^*, a_3^*, \ldots] \begin{bmatrix} \hat{O}_{11} & \hat{O}_{12} & \hat{O}_{13} & \cdots \\ \hat{O}_{21} & \hat{O}_{22} & \hat{O}_{23} & \cdots \\ \hat{O}_{31} & \hat{O}_{32} & \hat{O}_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \qquad [7.39]$$

We have actually used the infinite series expansion of the wave function in terms of an orthogonal set of eigenfunctions for the first time in connection with the perturbation methods discussed in chapter 6. We can now rewrite [6.36] using the more general notation discussed in this section. Taking the first line of [6.36] we obtain

$$\begin{bmatrix} a_1^{(1)} \\ a_2^{(1)} \\ a_3^{(1)} \\ \vdots \end{bmatrix} = \begin{bmatrix} 1 & \hat{O}_{12} & \hat{O}_{13} & \cdots \\ \hat{O}_{21} & 1 & \hat{O}_{23} & \cdots \\ \hat{O}_{31} & \hat{O}_{32} & 1 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix} \qquad [7.40]$$

where

$$\hat{O}_{21} = \frac{O'_{21}}{A^2(O_1^0 - O_2^0)}$$

$$\hat{O}_{31} = \frac{O'_{31}}{A^2(O_1^0 - O_3^0)} \tag{7.41}$$

and so on. In the column matrix on the right of [7.40] all $a_i = 0$, except $a_1 = 1$; they are the components of I_1^0 when the coordinates are the eigenfunctions I_i^0. This vector is transformed by the matrix operator $\hat{O}_{ij}$ into another vector $[a_i^{(1)}]$, which represents the wave function I_1 corresponding to the lowest harmonic of the perturbed system. Similarly, if we took the second line of [6.36] of chapter 6 this would give us the transformation of the initial vector representing I_2^0, into a new vector $[a_i^{(2)}]$ representing the second harmonic of the perturbed system I_2, and so on. In this case, the notation of [6.36] is more concise, but at the same time it is less general.

The simplest example of a matrix operator is probably that of the position operator $\hat{O} = \hat{q}$. Substituting this in (7.38) and choosing $\zeta_i = \Psi_i^0(q, t)$, where $\Psi_i^0(q, t)$ form the complete orthonormal set of the time-dependent energy eigenfunctions of the system, we obtain

$$\hat{q} = \begin{bmatrix} \hat{q}_{11} & \hat{q}_{12} & \hat{q}_{13} & \cdots \\ \hat{q}_{21} & \hat{q}_{22} & \hat{q}_{23} & \cdots \\ \hat{q}_{31} & \hat{q}_{32} & \hat{q}_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix}$$

$$= [\hat{q}_{ij}]$$

$$= [q_{ij}\, e^{j(E_i - E_j)t/\hbar}]$$

$$= [q_{ij}\, e^{j\omega_{ij}t}] \tag{7.42}$$

where

$$q_{ij} = \int \psi_i^* \hat{q} \psi_j \, d\tau \tag{7.43}$$

In a similar manner, we can derive a matrix operator for the linear momentum p, so that

$$\hat{p} = [\hat{p}_{ij}]$$

$$= [p_{ij}\, e^{j(E_i - E_j)t/\hbar}]$$

$$= [p_{ij}\, e^{j\omega_{ij}t}] \tag{7.44}$$

where now

$$p_{ij} = \int \psi_i^* \hat{p} \psi_j \, d\tau \tag{7.45}$$

This representation, arrived at differently, was in fact used by Heisenberg and others[13] in the early development of matrix mechanics, before Schrödinger's wave approach was known. The angular frequencies ω_{ij} appearing in [7.42] and [7.44] correspond to the experimentally observable lines of an atomic spectrum. The diagonal terms of both matrices give the mean values of the variables when the system is in an eigenstate, the off-diagonal terms being related to the probability of transitions.

We can now find the matrix representation of the Hamilton equations of motion. Substituting matrices for operators in (3.83a and b) we obtain, for a one-dimensional system,

$$\frac{\mathrm{d}[\hat{q}_{ij}]}{\mathrm{d}t} = \frac{j}{\hbar}([\hat{H}_{ik}][\hat{q}_{kj}] - [\hat{q}_{ik}][\hat{H}_{kj}])$$

$$\frac{\mathrm{d}[\hat{p}_{ij}]}{\mathrm{d}t} = \frac{j}{\hbar}([\hat{H}_{ik}][\hat{p}_{kj}] - [\hat{p}_{ik}][\hat{H}_{kj}])$$

[7.46]

where the elements of $[\hat{H}_{ij}]$ are the usual functions of $[\hat{q}_{ij}]$ and $[\hat{p}_{ij}]$. Now all elements, except those along the diagonal, must be functions of time. Since in a conservative system the Hamiltonian does not depend on time, this particular representation requires that such a Hamiltonian should be a diagonal matrix.

By analogy with (3.69), we can also show the non-commutating property of the two matrices representing the canonical coordinate operators $[\hat{q}_{ij}]$ and $[\hat{p}_{ij}]$, namely,

$$[\hat{q}_{ik}][\hat{p}_{kj}] - [\hat{p}_{ik}][\hat{q}_{kj}] = j\hbar[\delta_{ij}]$$

[7.47]

where $[\delta_{ij}]$ is the usual Kronecker delta matrix, consisting of zeros except for the diagonal terms which are all equal to unity (this matrix is also called the unit or idem matrix and written $[I]$).

Let us now consider the problem of eigenvalues and eigenfunctions and their appropriate representation in terms of matrices. Expressing the wave function Ψ of the eigenvalue equation (3.65) in terms of series (7.32), where (3.65) could represent, for example, the Schrödinger equation (3.65a), we obtain

$$\hat{O}\sum_i a_i \zeta_i = O \sum_i a_i \zeta_i$$

Multiplying both sides of this equation by ζ_j^* and integrating, i.e., taking the inner product, we obtain

$$\int \sum_i a_i \zeta_j^* \hat{O} \zeta_i \, \mathrm{d}z = O \int \sum_i a_i \zeta_j^* \zeta_i \, \mathrm{d}z$$

which, in view of the orthonormal properties of the functions ζ_i, reduces

to the following expression

$$\sum_i a_i \hat{O}_{ji} = O a_j \tag{7.48}$$

We can write this in matrix notation as

$$[\hat{O}_{ji}][a_i] = O[a_j]$$

or as

$$\begin{bmatrix} \hat{O}_{11}-O & \hat{O}_{12} & \hat{O}_{13} & \cdots \\ \hat{O}_{21} & \hat{O}_{22}-O & \hat{O}_{23} & \cdots \\ \hat{O}_{31} & \hat{O}_{32} & \hat{O}_{33}-O & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} = 0 \qquad [7.48]$$

This represents an infinite set of linear, homogeneous equations for the eigenvectors $[a_i]$ or more clearly $[a_i^{(j)}]$, each vector corresponding to a different eigenfunction Ψ_j of the system. A nontrivial solution of [7.48] exists only when the determinant of the matrix is zero, i.e., when

$$|\hat{O}_{ji} - O\delta_{ji}| = 0 \tag{7.49}$$

the roots of this determinant being the eigenvalues of the system. If the arbitrary set of orthonormal coordinate functions (or basis) ζ_i happens to be the orthonormal set of eigenfunctions of the system ψ_i, then, by definition, the eigenvalue equation is satisfied for each eigenfunction separately and we obtain

$$\sum_i a_i O_{ji} \delta_{ji} = O_j a_j \tag{7.50}$$

since now $a_i^{(j)}=1$ when $i=j$ and $a_i^{(j)}=0$ when $i \neq j$ and O_j's are the respective eigenvalues of the system. (The superscript (j) differentiates between a_i's belonging to different eigenvectors Ψ_j.) Rewriting (7.50) in matrix notation we find that [7.48] now reduces to

$$\begin{bmatrix} \hat{O}_{11}-O_1 & 0 & 0 & \cdots \\ 0 & \hat{O}_{22}-O_2 & 0 & \cdots \\ 0 & 0 & \hat{O}_{33}-O_3 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} = 0 \qquad [7.50]$$

Thus, in terms of matrix mechanics, the solution of an eigenvalue equation such as the important time-independent Schrödinger equation, amounts to the diagonalization of the corresponding matrix operator $[\hat{O}_{ij}]$ by a transformation of coordinates from an arbitrary basis to that coinciding with the correct eigenfunctions of the system. Such a transformation must retain the normalization and the orthogonality properties

of the coordinate functions and is called a unitary transformation.[14] Thus, in matrix mechanics, the equivalent of solving an eigenvalue equation is the discovery of a suitable unitary transformation which diagonalizes the corresponding matrix operator $[\hat{O}_{ij}]$. Such a transformation also keeps constant the trace of the matrix, i.e., the sum of its diagonal terms which, in the case of a diagonal matrix, is equal to the sum of all its eigenvalues. This is not surprising because the diagonalization of a matrix, which amounts to a suitable rotation in Hilbert space, should not alter its eigenvalues.

An identical procedure could be applied to the solution of many problems concerning the behaviour of an oscillating system.[15] In electrical engineering we often express the behaviour of such a system in terms of its normal modes.[16] Such modes are completely decoupled and thus, when expressed in matrix form, lead to a diagonal matrix of the type [7.50].

As the last example of matrix representation, let us now consider the time-dependent Schrödinger equation (7.1). Expressing the wavefunction in the form of a series, we obtain from (7.32)

$$jh \sum_i \dot{a}_i \zeta_i = \sum_i a_i \hat{H} \zeta_i$$

Taking the inner product, i.e., multiplying both sides of the equation by ζ_j^* and integrating with respect to z we obtain, in view of the orthonormal properties of the set ζ_i

$$jh \int \sum_i \dot{a}_i \zeta_j^* \zeta_i \, dz = \sum_i a_i \int \zeta_j^* \hat{H} \zeta_i \, dz$$

$$jh \dot{a}_j = \sum_i \hat{H}_{ji} a_i \qquad (7.51)$$

where

$$\hat{H}_{ji} = \int \zeta_j^* \hat{H} \zeta_i \, dz \qquad (7.52)$$

or

$$jh \begin{bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} \hat{H}_{11} & \hat{H}_{12} & \hat{H}_{13} & \cdots \\ \hat{H}_{21} & \hat{H}_{22} & \hat{H}_{23} & \cdots \\ \hat{H}_{31} & \hat{H}_{32} & \hat{H}_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix} \qquad [7.51]$$

If we choose for ζ_i the time-dependent energy eigenfunctions and if the Hamiltonian operator can be separated into a time-independent part $\hat{H}^0$ and a time-dependent part $\hat{H}'(t)$, then [7.51] reduces exactly to [7.7],

where $\bar{H}'_{ij}$ is used for $\hat{H}_{ij}$. In general, the use of the time-dependent energy eigenfunctions $\Psi_i(z, t)$ as the basis $\zeta_i(z)$ gives rise to a matrix operator whose terms are functions of time, as can be seen from (7.38), except for the diagonal, where the two exponential terms cancel. This forms the so-called Heisenberg representation, where an operator which does not depend on time must be represented by a diagonal matrix. Heisenberg's representation dates to the early days of quantum mechanics and was used in the original derivation of [7.42]–[7.47].

Let us now consider a time-independent Hamiltonian operator $\hat{H}$ which is expressed however in terms of its time-independent energy eigenfunctions $\psi_i(z)$. Then, since the basis ζ_i now consists of the eigenfunctions of the operator, the matrix operator $[\hat{H}_{ij}]$ must be diagonal as in [7.50] and [7.51] reduces to

$$
j\hbar
\begin{bmatrix}
\dot{a}_1 \\
\dot{a}_2 \\
\dot{a}_3 \\
\vdots
\end{bmatrix}
=
\begin{bmatrix}
\hat{H}_{11} & 0 & 0 & \cdots \\
0 & \hat{H}_{22} & 0 & \cdots \\
0 & 0 & \hat{H}_{33} & \cdots \\
\vdots & \vdots & \vdots &
\end{bmatrix}
\begin{bmatrix}
a_1 \\
a_2 \\
a_3 \\
\vdots
\end{bmatrix}
$$

$$
=
\begin{bmatrix}
E_1 & 0 & 0 & \cdots \\
0 & E_2 & 0 & \cdots \\
0 & 0 & E_3 & \cdots \\
\vdots & \vdots & \vdots &
\end{bmatrix}
\begin{bmatrix}
a_1 \\
a_2 \\
a_3 \\
\vdots
\end{bmatrix}
\qquad [7.53]
$$

This set of equations can be solved quite readily giving, in general,

$$
a_i(t) = e^{-jE_i t/\hbar} \tag{7.54}
$$

since all $a_i(0) = 1$. From (7.32) the wave functions now become

$$
\Psi_j(z, t) = \sum_i a_i^{(j)}(t)\psi_i(z)
$$

$$
= a_j^{(j)}(t)\psi_j(z)
$$

$$
= \psi_j(z) e^{-jE_j t/\hbar} \tag{7.55}
$$

as would be expected, since $\psi_i(z)$ are the time-independent energy eigenfunctions of the system by definition. It should be noted, however, that in computing averages, (7.39), it makes no difference whether we incorporate the factors $\exp(-jE_i t/\hbar)$ in a_i's, as in the Schrödinger representation, or in $\hat{O}_{ij}$'s, as in the Heisenberg representation. In each case we obtain the same value for the observables, although it can be argued that in the Heisenberg representation, the calculations are carried out more in terms of the actual observables than in the other case. From the geo-

metrical point of view we could say that in the Schrödinger representation the behaviour of a system is described by some complicated rotation of the wave function vector in a fixed coordinate frame, the time-dependent operator remaining stationary, whereas in the Heisenberg representation the coordinates are made to rotate with the wave function vector, so that the operator now appears to rotate in the opposite direction, even though it does not explicitly depend on time. If it does, however, we can then write in the Heisenberg representation in terms of the time-dependent energy eigenfunctions $\Psi_i(z, t)$

$$\frac{\mathrm{d}\hat{O}_{ij}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int \Psi_i^* \hat{O} \Psi_j \, \mathrm{d}z$$

$$= \frac{j}{\hbar}(E_i - E_j) \int \psi_i^* \, \mathrm{e}^{jE_i t/\hbar} \hat{O} \psi_j \, \mathrm{e}^{-jE_j t/\hbar} \, \mathrm{d}z + \int \psi_i^* \, \mathrm{e}^{jE_i t/\hbar} \frac{\partial \hat{O}}{\partial t} \psi_j \, \mathrm{e}^{-jE_j t/\hbar} \, \mathrm{d}z$$

$$= \frac{j}{\hbar}(E_i - E_j)\hat{O}_{ij} + \left(\frac{\partial \hat{O}}{\partial t}\right)_{ij} \tag{7.56}$$

But for a conservative system, the only type of system considered here, the Hamiltonian operator $[\hat{H}_{ij}]$ in the Heisenberg representation must be diagonal, so that $E_i = \hat{H}_{ii}$ and $E_j = \hat{H}_{jj}$ and we can write, substituting in (7.56),

$$\frac{\mathrm{d}\hat{O}_{ij}}{\mathrm{d}t} = \frac{j}{\hbar}(\hat{H}\hat{O} - \hat{O}\hat{H})_{ij} + \left(\frac{\partial \hat{O}}{\partial t}\right)_{ij} \tag{7.57}$$

Since (7.57) must be valid for all elements of the matrix operator $[\hat{O}_{ij}]$, we obtain, in general,

$$\frac{\mathrm{d}[\hat{O}_{ij}]}{\mathrm{d}t} = \frac{j}{\hbar}([\hat{H}_{ik}][\hat{O}_{kj}] - [\hat{O}_{ik}][\hat{H}_{kj}]) + \left[\left(\frac{\partial \hat{O}}{\partial t}\right)_{ij}\right] \tag{7.58}$$

This shows that an operator $[\hat{O}_{ij}]$ can be a constant of motion, i.e., $\mathrm{d}[\hat{O}_{ij}]/\mathrm{d}t = 0$, only when it commutes with the Hamiltonian operator $[\hat{H}_{ij}]$. Since for a conservative system $[\hat{H}_{ij}]$ is diagonal it means that the operator itself must be a diagonal matrix as well. Substituting $[\hat{O}_{ij}] = [\hat{q}_{ij}]$ or $[\hat{O}_{ij}] = [\hat{p}_{ij}]$ we immediately obtain [7.46], which was previously obtained by a plausible analogy only. We can now see that [7.58] is indeed the exact matrix equivalent of (3.82), as we have rightly suspected. It should be noted, however, that, because of the substitution used in (7.56), this similarity only holds for matrix operators using the Heisenberg representation.

In general, one can say that either wave or matrix representation is acceptable in quantum mechanics; sometimes it is more convenient to discuss the problem using one, sometimes the other. In terms of matrices and vectors the development of a system in time can be represented as a

complicated rotation in Hilbert space, so that the whole of quantum mechanics can be reduced, in principle, to the study of the geometrical properties of Hilbert space; although such an approach is intellectually very elegant and quite general, it is not the easiest to apply in practice. A detailed discussion of the physical reality behind matrix representation can be found elsewhere.[17] In section 16.8 of the same reference the extension of matrix mechanics to systems characterized by continuous spectra is presented; this generalization was originally developed by Dirac[18] who, it is interesting to note, invented the Dirac or δ function in the process.

Problems

1. Explain in your own words why a stationary state cannot be directly observed. Is this in any way related to Heisenberg's uncertainty principle?

2. In view of (5.35), explain why it is necessary for the coefficients a_i to be time dependent in (7.3).

3. Derive (7.7) from (7.6) without using the summation sign.

4. What do we mean physically by a step function perturbation? Suggest a simple example.

5. Show that, to the first approximation, $a'_m = 0$ in the problem considered in section 7.2. Is this a general rule and if so, why?

6. Justify mathematically the statement concerning the behaviour of (7.15) at $\omega_{km} = 0$. State the assumptions restricting the validity of (7.15).

7. Sketch the perturbation function (7.16). How does it differ from the corresponding perturbation function of section 7.2? Sketch $a_k'^* a_k'$, starting from (7.19). Discuss the physical significance of the curve. Why are harmonic perturbation functions important in physics?

8. Calculate H'_{40} and H'_{13} for electric dipole transitions using suitable expressions for Hermite polynomials — see (4.43) and (4.46). Does this result surprise you? Would you expect the same result if the potential well were not parabolic?

9. Discuss the differences and similarities between (7.32) and (7.33). When $i \to \infty$, as it does in this case, would you expect the size or norm of the vectors given by $\sum_i a_i^2$ to be always finite? (In quantum mechanics we only deal with finite norm vectors. Why?)

10. Write the coordinate functions ζ_i in the form (7.34). Compare the result with that obtained for a three-dimensional vector.

11. Why is it necessary to use adjoint matrices in [7.35], [7.36], and [7.39]? What would have happened if we used either simple transpose or simple complex conjugate matrices instead?

12. Write (7.37) and (7.38) in full without using the summation sign. Do the same in the case of (7.39).

13. Derive an expression similar to [7.40] for I_3.

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8. Systems Comprising more than One Particle. Identical Particles

So far we have been considering one-particle systems only, but in practice it is more usual to encounter systems comprising many particles. This requires a generalization of the concept of wave function which is both fundamental and far-reaching in scope.

8.1. Definition of Ψ for N particles

Assume that Ψ represents the wave function defining a dynamic state of a system comprising N particles, so that $\Psi^*\Psi$ is the corresponding position probability density function of the particles. For a single particle the probability of finding it in an element of volume $d\mathbf{r} = dx\,dy\,dz$ is given by $\Psi^*\Psi\,d\mathbf{r} = \Psi^*\Psi\,dx\,dy\,dz$, where Ψ must be a function of the three space variables x, y, z. When the system comprises two particles, however, the probability of finding the first particle in the volume element $d\mathbf{r}_1$ and the second particle, simultaneously, in the volume element $d\mathbf{r}_2$ is given by $\Psi^*\Psi\,d\mathbf{r}_1\,d\mathbf{r}_2$, so that now Ψ must be a function of six space variables x_1, y_1, z_1 and x_2, y_2, z_2, or $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$. Similarly, for a system comprising N particles, the wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$, now being a function of $3N$ independent variables. Normalizing $\Psi^*\Psi$ we obtain in the case of two particles (six-dimensional space)

$$\iint \Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 = 1 \tag{8.1}$$

and in the case of N particles ($3N$-dimensional space)

$$\iint \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\,d\mathbf{r}_1\,d\mathbf{r}_2\cdots d\mathbf{r}_N = 1 \tag{8.2}$$

Equations (8.1) and (8.2) express the fundamental property of all probability density functions (see appendix 3) which physically represents certainty of finding the particles somewhere in the system.

The fact that Ψ in a system of N particles is a function of $3N$ variables, adds considerably to the algebraic complexity of such problems. Of

course, this is not peculiar to quantum mechanics, but merely represents the usual computational difficulties when more than a single particle has to be considered. However, if there is no interaction of any kind between the particles, the position of a single particle is completely independent of the position of all other particles and the joint probability density function $\Psi^*\Psi$ divides into a product of N functions, each depending only on three variables, the three position variables of a single particle (see (A3.14) in appendix 3 for the case of a probability density function of two independent variables). It is then sometimes convenient to normalize the function $\Psi^*\Psi$ to N rather than to unity, especially if the particles can be in n different energy states. The main advantage of this new normalization procedure is that the products $\Psi_n^*\Psi_n$ directly give the number of particles in any given energy state n.

8.2. Identical particles—general comments

One of the salutary features of quantum mechanics is its insistence on accurate thinking. Thus, if two particles are really identical, then there is no conceivable way of distinguishing between them. In classical mechanics, we can distinguish, in principle, between identical particles by first 'labelling' them and then following each particle along its own trajectory. This is no longer possible in quantum mechanics, since the mere process of labelling, if it is to be observed, must involve some change in the properties of the particles, so that by definition they cease to be identical. This difference in approach radically affects statistical considerations, as we shall see later. In the classical or Boltzmann statistics of identical particles (see appendix 5), we are allowed to assume, in the derivation of the energy distribution function, that it is possible to distinguish between individual particles, at least to the extent of being able to tell which particles, and not merely how many, are in a given energy class. In quantum statistics, this is no longer possible, since it would involve a form of labelling. As we shall see in the last two sections of this chapter, this change leads to new distributions called Bose–Einstein or Fermi–Dirac, depending on further details.

8.3. Two identical particles—exchange degeneracy

Let us now discuss the mathematical consequences of the basic assumption that on the atomic scale the particles are truly indistinguishable. Consider two particles of mass m_0 contained in an infinitely deep, one-dimensional potential well of width l. Then, from (A4.2) of appendix 4, the corresponding Schrödinger equation is given by

$$\frac{\hbar^2}{2m_0}\left(\frac{\partial^2\Psi}{\partial z_1^2}+\frac{\partial^2\Psi}{\partial z_2^2}\right)=j\hbar\frac{\partial\Psi}{\partial t} \tag{8.3}$$

Assume that the particles do not interact; now the potential energy

function does not depend on the relative position of the particles, $V(z_1, z_2) = V_\alpha(z_1) + V_\beta(z_2)$, and we have, inside the well,

$$V_\alpha(z_1) = V_\beta(z_2) = 0 \tag{8.4}$$

Furthermore, if the system is in a stationary state we can write for non-interacting particles

$$\Psi(z_1, z_2, t) = \psi(z_1)\psi(z_2)\psi_t(t) \tag{8.5}$$

Substituting (8.5) in (8.3) we obtain from (4.15),

$$\psi_t(t) = e^{-jEt/\hbar} \tag{8.6}$$

and

$$\frac{d^2\psi_\alpha}{dz_1^2} + \frac{2m_0}{\hbar^2} E_\alpha \psi_\alpha = 0 \tag{8.7}$$

$$\frac{d^2\psi_\beta}{dz_2^2} + \frac{2m_0}{\hbar^2} E_\beta \psi_\beta = 0 \tag{8.8}$$

where

$$E = E_\alpha + E_\beta \tag{8.9}$$

But we know from (5.9) and (5.10) that the solutions of (8.7), (8.8) are respectively given by two one-particle eigenfunctions

$$\psi_\alpha = \left(\frac{2}{l}\right)^{\frac{1}{2}} \sin \frac{m\pi}{l} z_1 \tag{8.10}$$

$$\psi_\beta = \left(\frac{2}{l}\right)^{\frac{1}{2}} \sin \frac{n\pi}{l} z_2 \tag{8.11}$$

where

$$E_\alpha = \frac{m^2 \pi^2 \hbar^2}{2m_0 l^2} \tag{8.12}$$

$$E_\beta = \frac{n^2 \pi^2 \hbar^2}{2m_0 l^2} \tag{8.13}$$

We now find from (8.5) and (8.9) that the time-independent part of the zero order energy eigenfunctions and the energy eigenvalues of a system consisting of two non-interacting particles bound in an infinitely deep potential well of width l are given by

$$\psi_{12}^0(z_1, z_2) = \frac{2}{l} \sin \frac{m\pi}{l} z_1 \sin \frac{n\pi}{l} z_2$$

$$= \psi_\alpha(1)\psi_\beta(2) \tag{8.14}$$

$$\psi_{21}^0(z_1, z_2) = \frac{2}{l} \sin \frac{m\pi}{l} z_2 \sin \frac{n\pi}{l} z_1$$

$$= \psi_\alpha(2)\psi_\beta(1) \tag{8.15}$$

$$E^0 = \frac{(m^2 + n^2)\pi^2\hbar^2}{2m_0 l^2} \tag{8.16}$$

either of the two functions satisfying (8.3) when multiplied by $\psi_t(t)$ of (8.6). (It is customary to write $\psi_\alpha(z_1) \equiv \psi_\alpha(1)$, $\psi_\alpha(z_2) \equiv \psi_\alpha(2)$, etc., for brevity.)

Equations (8.14) and (8.15) clearly show that the system is degenerate, since, whenever $m \neq n$, to each eigenvalue E^0 correspond two different two-particle eigenfunctions ψ_{12}^0 and ψ_{21}^0. This so-called *exchange degeneracy* is solely due to the fact that the two particles are quite indistinguishable, their mass m_0 being exactly the same. The zero order functions ψ_{12}^0 and ψ_{21}^0 for $m = 1$ and $n = 2$ are shown respectively in Figs. 8.1 and 8.2.
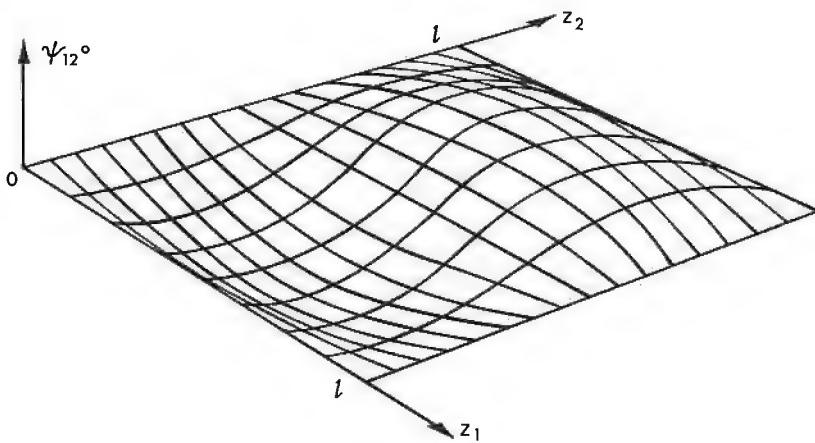
Fig. 8.1. Two-particle eigenfunction $\psi_{12}^0(z_1, z_2)$; $m = 1$, $n = 2$.

Let us now perturb the system by allowing the particles to interact, though only slightly. For example, we could assume that both particles possess electric charge q, when the perturbation operator would be given by

$$\hat{H}' = \frac{q^2}{4\pi\varepsilon_0 z_{12}} \tag{8.17}$$

Here $z_{12} = |z_2 - z_1|$ is the separation between the particles and does not depend on the order of labelling the coordinates in the so-called 'configuration space' (z_1, z_2). Since, when $m \neq n$, the corresponding energy

state is degenerate, $\psi_{12}^0 \neq \psi_{21}^0$ for the same E^0, we can apply the perturbation procedure for degenerate states developed in section 6.6. Fortunately, the functions ψ_{12}^0 and ψ_{21}^0 are already orthogonal so that we can write directly, putting $\psi_{12}^0 = \psi_c^0$, $\psi_{21}^0 = \psi_d^0$ for convenience (see (6.69)),

$$\psi_{cd}^0 = b_c \psi_c^0 + b_d \psi_d^0 \tag{8.18}$$

where, as usual,

$$b_c^* b_c + b_d^* b_d = 1 \tag{8.19}$$
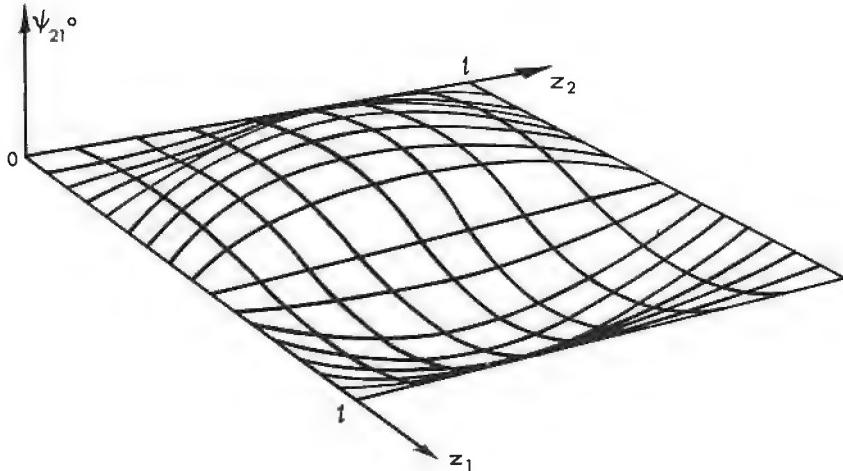
Fig. 8.2. Two-particle eigenfunction $\psi_{21}^0(z_1, z_2)$; $m=1$, $n=2$.

Following (6.75) and (6.76) the two equations relating b_c and b_d are

$$0 = b_c E' - b_c H_{cc}' - b_d H_{cd}' \tag{8.20}$$

$$0 = b_d E' - b_c H_{dc}' - b_d H_{dd}' \tag{8.21}$$

and we obtain for the secular equation [6.78],

$$\begin{vmatrix} H_{cd}' - E' & H_{cd}' \\ H_{dc}' & H_{dd}' - E' \end{vmatrix} = 0 \tag{8.22}$$

where, as usual,

$$H_{ij}' = \int \psi_i^{0*} \hat{H}' \psi_j^0 \, dz \tag{8.23}$$

But, in our case, from (8.14), (8.15), and (8.17)

$$H_{cc}' = H_{dd}' \tag{8.24}$$

$$H_{cd}' = H_{dc}' \tag{8.25}$$

as we can readily see by substituting in (8.23), the corresponding integral being unaffected by renaming the variables, say $z_1 = z_2'$, $z_2 = z_1'$. Now [8.22] reduces to

$$(H'_{cc} - E')^2 = H'^2_{cd} \tag{8.26}$$

the two roots, i.e., the two correction terms to the eigenvalue E^0 being

$$E'_c = H'_{cc} + H'_{cd} \tag{8.27}$$

$$E'_d = H'_{cc} - H'_{cd} \tag{8.28}$$

Substituting E'_c and E'_d into (8.20), (8.21) we obtain

$$b_c^{(c)} = b_d^{(c)} \tag{8.29}$$

$$b_c^{(d)} = -b_d^{(d)} \tag{8.30}$$

where the superscripts indicate the two new wave functions ψ_c and ψ_d respectively, corresponding to the two new energy eigenvalues

$$E_c = E^0 + E'_c \tag{8.31}$$

$$E_d = E^0 + E'_d \tag{8.32}$$

From $(6.81m)$ and $(6.81n)$ we obtain the following complete expressions for the two eigenfunctions ψ_c and ψ_d of the new perturbed system,

$$\psi_c = b_c^{(c)}(\psi_c^0 + \psi_d^0) + \sum_i a_i^{(c)}\psi_i^0 \tag{8.33}$$

$$\psi_d = b_c^{(d)}(\psi_c^0 - \psi_d^0) + \sum_i a_i^{(d)}\psi_i^0 \tag{8.34}$$

where $i \neq c, d$.

We have seen in chapter 6 that although E', ψ', and a_i all tend to zero as the operator $\hat{H}' \to 0$, the b coefficients do not. Thus, in the limit $a_i \to 0$, (8.33) and (8.34) give the zero order eigenfunctions appropriate to a system which, when the particles interact, would be described by a perturbation operator which is symmetric to the interchange of the two variables z_1 and z_2, such as $\hat{H}'$, of (8.17); such wave functions have to be used in place of (8.14), (8.15) even in the first order calculations. Substituting (8.29), (8.30) in the normalization equation (8.19) we obtain

$$|b_c^{(c)}| = \frac{1}{\sqrt{2}} \tag{8.35}$$

$$|b_d^{(d)}| = \frac{1}{\sqrt{2}} \tag{8.36}$$

to within an undetermined phase angle which would in any case disappear in all calculations of observables (see (3.66)). From (8.33)–(8.36)

we obtain for the zero order approximation

$$\psi_S = \frac{1}{\sqrt{2}} (\psi_c^0 + \psi_d^0)$$

$$= \frac{\sqrt{2}}{l} \left(\sin \frac{m\pi}{l} z_1 \sin \frac{n\pi}{l} z_2 + \sin \frac{m\pi}{l} z_2 \sin \frac{n\pi}{l} z_1 \right)$$

$$= \frac{1}{\sqrt{2}} \{ \psi_\alpha(1)\psi_\beta(2) + \psi_\alpha(2)\psi_\beta(1) \} \tag{8.37}$$

$$\psi_A = \frac{1}{\sqrt{2}} (\psi_c^0 - \psi_d^0)$$

$$= \frac{\sqrt{2}}{l} \left(\sin \frac{m\pi}{l} z_1 \sin \frac{n\pi}{l} z_2 - \sin \frac{m\pi}{l} z_2 \sin \frac{n\pi}{l} z_1 \right)$$

$$= \frac{1}{\sqrt{2}} \{ \psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1) \} \tag{8.38}$$

Since the eigenfunction ψ_S retains its sign when the variables z_1 and z_2 are interchanged, it is called *symmetric*; for ψ_A the sign changes and it is called *antisymmetric*. When the two particles are in different energy states, $c \neq d$, the eigenfunctions can be either symmetric or antisymmetric, but when they are in the same energy state, $c = d$, the corresponding eigenfunctions must be symmetric, as can be seen from (8.37), (8.38). Conversely, if we know from other considerations that the particles must be associated with antisymmetric wave functions, this implies that they cannot coexist in the same energy state, a situation which has very important consequences, for example, in the construction of electronic shells in atoms, according to Pauli's exclusion principle. Since from (8.10), (8.11) the energy states $c = d$ are non-degenerate, only one eigenfunction belonging to the energy level E^0 given by (8.16), the two-particle eigenfunctions (8.14), (8.15) can then be used directly in other perturbation calculations, no need now arising for forming a linear combination of the type (8.18).

Finally, by investigating the form of a_i's (see (6.80m) and (6.80n)) it can be shown that the wave functions ψ_c and ψ_d of (8.33), (8.34) are again either symmetric or antisymmetric, so that the introduction of particle interaction does not destroy this property of the wave functions. More generally, if a particle is associated with one particular type of wave function, this cannot be changed by forces acting on it, a fact which depends on the symmetry properties of the perturbation operators $\hat{H}'$ relating to particle interactions. Experimental evidence tells us that electrons, protons, and neutrons are associated with antisymmetric wave functions, whereas α-particles and photons are associated with symmetric wave functions.

Let us now consider the two joint probability density functions associated with the symmetric and antisymmetric wave functions ψ_S and ψ_A, as shown in Figs. 8.3 and 8.4. These drawings look deceptively straightforward, but since they are plotted in configuration rather than physical space, the physical meaning of the corresponding probability calculations is quite startling. We find from (A3.8) of appendix 3, that the joint probability of finding particle 1 in the interval dz_1 centred on z_1 and particle 2 in the interval dz_2 centred on z_2 is given by $\Psi^*\Psi \, dz_1 \, dz_2$. In
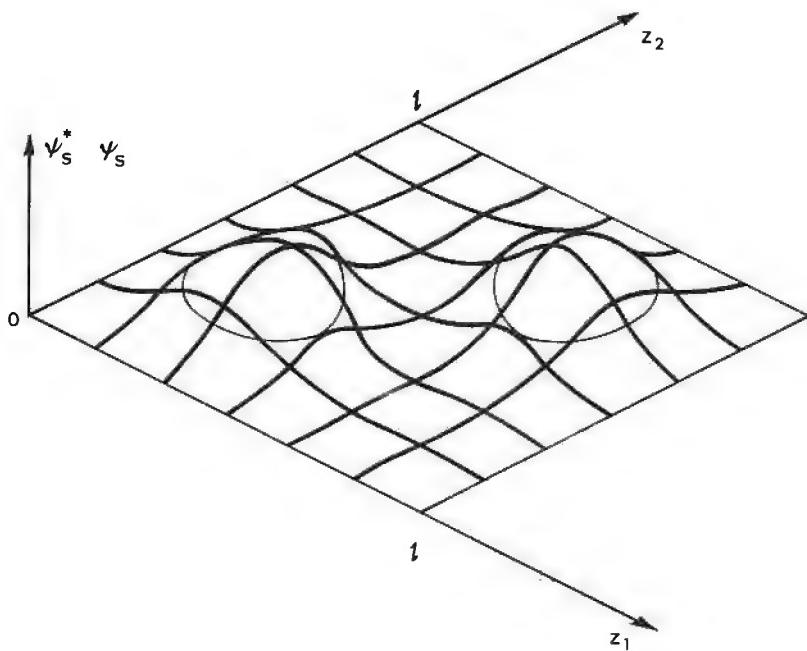
Fig. 8.3. Two-particle probability density function $\psi_S^* \psi_S$.

the case of particles represented by symmetric wave functions ψ_S, the peaks of $\psi_S^* \psi_S$ occur along the line $z_1 = z_2$, i.e., the probability of finding the two particles together either at $z_1 = z_2 = \frac{1}{4}l$ or at $z_1 = z_2 = \frac{3}{4}l$ is quite high. In other words, even in the zero-order approximation, when the interaction represented by the operator $\hat{H}'$ is assumed to be zero, the particles associated with symmetric wave functions tend to 'stick together'. Such particles, when considered in large numbers, follow the so-called Bose–Einstein statistics and are often called bosons. The situation is quite different however for the particles which are associated with antisymmetric wave functions. Now we can see from Fig. 8.4 that the new maxima of the probability density function occur along the other diagonal of the $l \times l$ square. This means that when particle 1 is in the vicinity of

$\frac{1}{4}l$, particle 2 is likely to be in the vicinity of $\frac{3}{4}l$ and vice versa. Again, even in the zero-order approximation, i.e., when the perturbation operator $\hat{H}' = 0$ and no interaction forces are present, the particles still tend to 'shun' each other; on the average they are less often together than would have been predicted on the basis of classical mechanics. When in large numbers, such particles obey the so-called Fermi–Dirac statistics and are often referred to as fermions. We shall see in chapter 9 that this behaviour is characteristic of electrons. It should be added that the 'sticking' together of particles associated with symmetric wave functions gives rise
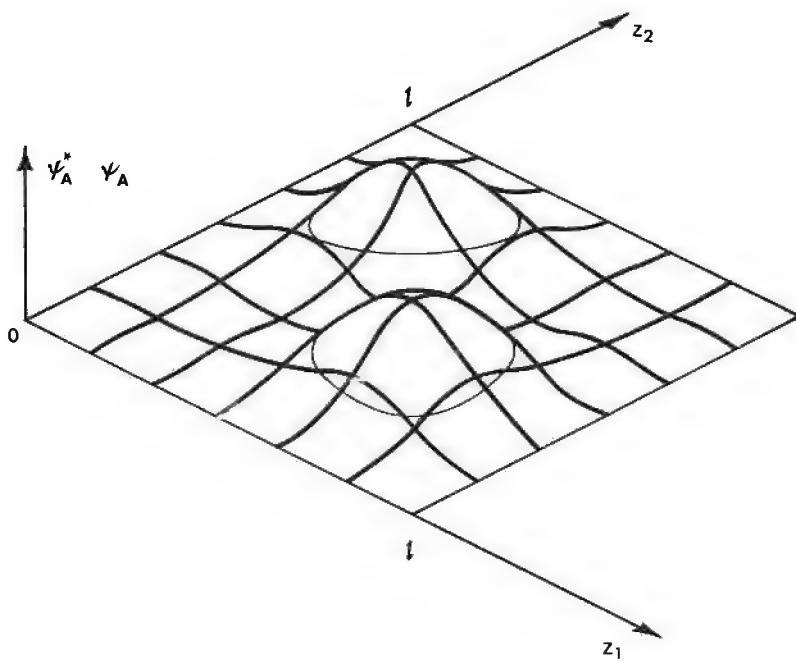
Fig. 8.4. Two-particle probability density function $\psi_A^* \psi_A$.

to the 'covalent bond' of chemical theory. On the other hand, the 'anti-social' behaviour of electrons gives rise to the shell structure of the atom and hence to the periodic table of the elements; if it were not for the fact that the electrons 'shun' each other, they would all be found in the lowest energy level, leaving the other levels of an atom quite empty. Pauli's exclusion principle, which is so important in the construction and under-standing of electronic shells, relies on this unusual property of the electrons. Of course the question of symmetry or antisymmetry of particles only arises when their wave functions overlap, as they do for example in the case of two electrons bound in the same potential well.

If this is not the case, the off-diagonal coefficients H'_{cd} vanish even when the perturbation operator $\hat{H}' \neq 0$, since then the wave function of one particle is zero where the wave function of the other particle is not and vice versa, the system no longer being exchange degenerate. Such situations are, however, very rare in practice, because unless the barriers between the particles can be assumed to be sufficiently large, the corresponding wave functions spread, the amplitudes remaining different from zero, though exceedingly small, over large distances. The exchange degeneracy does not disappear until the overlap becomes exactly zero.

8.4. Bose–Einstein statistics

When the number of particles is large it is impractical to adopt the rigorous approach of section 8.1 and, just as in classical mechanics, one is forced to adopt statistical methods. The classical law of energy distribution valid for a system which is in equilibrium and contains a large number of non-interacting particles has been derived in appendix 5. It is now necessary to amend this law in the light of the new principles developed in quantum mechanics. Bosons will be considered in this section and fermions in the next, the two types of particle being respectively associated with symmetric and antisymmetric wave functions.[1]

We have already pointed out in section 8.1 that, in general, the dynamic state of a system comprising N particles can be fully described only by a wave function of $3N$ position variables (and time). However, when the particles are non-interacting the wave function divides into a product of N independent wave functions of three position variables each (and time). These functions may not necessarily be the same even for identical particles, since the particles may be in different energy states.

Let us now consider a subsystem consisting of only those particles which are in the same energy state. Dividing the phase space τ, i.e., the space in which position and momentum variables are treated as independent (see appendix 5), into a large number of small cells τ_i, we now describe the dynamic state of such a subsystem by specifying a cell distribution function $\mathcal{N}_n$, where $\mathcal{N}_0$ is the number of empty cells, $\mathcal{N}_1$ is the number of cells containing a single particle, $\mathcal{N}_2$ is the number of cells containing two particles and so on, as shown in Fig. 8.5. However, if for a given energy, the cells are only labelled by the number of particles n they contain, the distribution will not be altered by their rearrangement; for example, if cell A contains three particles and thus belongs to the group $\mathcal{N}_3$ and cell B contains five particles and thus belongs to the group $\mathcal{N}_5$, their groups and labels can be interchanged without affecting the distribution $\mathcal{N}_n$ in any way. We define the likelihood of a given distribution $\mathcal{N}_n$ by the number of such possible rearrangements.

If all cells contain different numbers of particles, then they can be rearranged in $\mathcal{N}!$ different ways, the likelihood of such state being $W = \mathcal{N}!$. If several cells have the same number of particles, say three, then they acquire the same label and their interchange no longer counts as a new arrangement, the likelihood of the corresponding state now being reduced by the factor $\mathcal{N}_3!$. In general, the likelihood of an arbitrary state is given by

$$W = \frac{\mathcal{N}!}{\mathcal{N}_1!\mathcal{N}_2!\cdots\mathcal{N}_n!\cdots} = \frac{\mathcal{N}!}{\prod_n \mathcal{N}_n!} \tag{8.39}$$

where $\mathcal{N} = \sum_n \mathcal{N}_n$ is the total number of cells and $N = \sum_n n\mathcal{N}_n$ is the total number of particles. Equation (8.39) should be compared to (A5.1) of appendix 5, giving the likelihood of a state based on classical considerations. The only difference is that in place of the number of particles
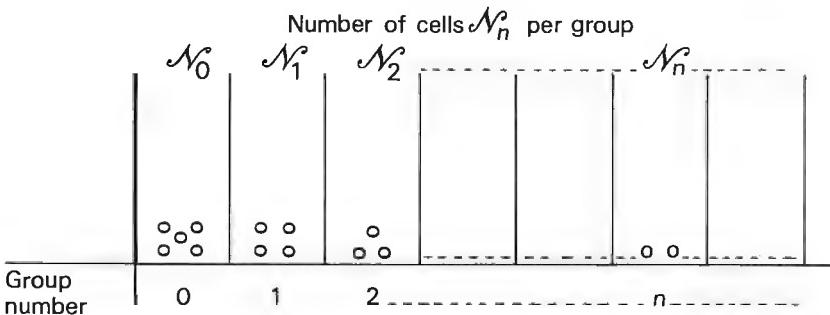
Fig. 8.5. Cell distribution in quantum mechanics.

N_i in a cell i we now have the number of cells $\mathcal{N}_n$ in a group labelled n, as shown in Figs. A5.1 and 8.5. This distinction was forced on us because in quantum mechanics identical particles remain indistinguishable and thus cannot be subjected to the labelling process described in appendix 5. Consequently, the corresponding energy distribution law will differ substantially from that derived by Boltzmann, as we shall see.

So far we have considered a subsystem comprising particles in the same energy state E_j. Since (8.39) must be true for all such subsystems, the joint likelihood of the whole system comprising identical particles in different energy states E_j is given by the product

$$W = W_1 W_2 \cdots W_j \cdots = \prod_j W_j = \prod_j \frac{\mathcal{N}_j!}{\prod_n \mathcal{N}_{nj}!} \tag{8.40}$$

Taking the logarithm of (8.40) we obtain

$$\ln W = \sum_j \ln W_j$$

$$= \sum_j \ln \mathcal{N}_j! - \sum_j \sum_n \ln \mathcal{N}_{nj}!$$

$$= \sum_j \mathcal{N}_j \ln \mathcal{N}_j - \sum_j \mathcal{N}_j - \sum_j \sum_n \mathcal{N}_{nj} \ln \mathcal{N}_{nj} + \sum_j \sum_n \mathcal{N}_{nj}$$

$$= \sum_j \mathcal{N}_j \ln \mathcal{N}_j - \sum_j \sum_n \mathcal{N}_{nj} \ln \mathcal{N}_{nj} \qquad (8.41)$$

where we have used the approximate expression (A5.3) of appendix 5 to obtain the third line.

In order to calculate the most likely distribution $\mathcal{N}_{nj}$, it is necessary to find the maximum of (8.41), subject to three constraints, namely, that the total number of cells in each energy group

$$\mathcal{N}_j = \sum_j \mathcal{N}_{nj} \qquad (8.42)$$

is fixed by the geometry of the system and that, in equilibrium, the total number of particles

$$N = \sum_j \sum_n n \mathcal{N}_{nj} \qquad (8.43)$$

and the total energy of the system

$$E = \sum_j \sum_n E_j n \mathcal{N}_{nj} \qquad (8.44)$$

remain constant.

Using the Lagrange's multipliers[2] we calculate the differences $\delta(\ln W)$, $\delta \mathcal{N}_j$, δN, and δE and equate them to zero

$$\delta(\ln W) = -\sum_j \sum_n \delta \mathcal{N}_{nj} \ln \mathcal{N}_{nj} - \sum_j \sum_n \delta \mathcal{N}_{nj}$$

$$= -\sum_j \sum_n \delta \mathcal{N}_{nj} (\ln \mathcal{N}_{nj} + 1) = 0 \qquad (8.45)$$

$$\delta \mathcal{N}_j = \sum_j \delta \mathcal{N}_{nj} = 0 \qquad (8.46)$$

$$\delta N = \sum_j \sum_n n \, \delta \mathcal{N}_{nj} = 0 \qquad (8.47)$$

$$\delta E = \sum_j \sum_n E_j n \, \delta \mathcal{N}_{nj} = 0 \qquad (8.48)$$

Multiplying (8.47) by α, (8.48) by β, and (8.46) by γ and subtracting them from (8.45) we obtain, since the equality must be satisfied for all n and j

$$\ln \mathcal{N}_{nj} + 1 + \alpha n + \beta E_j n + \gamma = 0 \qquad (8.49)$$

or

$$\mathcal{N}_{nj} = e^{-1-\gamma} e^{-n(\alpha + \beta E_j)} \qquad (8.50)$$

Substituting (8.50) back in (8.42) we obtain

$$\mathcal{N}_j = \sum_n \mathcal{N}_{nj} = e^{-1-\gamma} \sum_n e^{-n(\alpha + \beta E_j)}$$

$$= \frac{\exp(-1-\gamma)}{1 - \exp(-\alpha - \beta E_j)} \tag{8.51}$$

where the identity

$$\{1 - \exp(-x)\}^{-1} = 1 + \exp(-x) + \exp(-2x) + \exp(-3x) + \cdots$$

has been used. In order to calculate the number of particles N_j in each energy group E_j, we write, using (8.43), (8.50), and the summation of (8.51)

$$N_j = \sum_n n \mathcal{N}_{nj}$$

$$= \sum_n e^{-1-\gamma} n\, e^{-n(\alpha + \beta E_j)}$$

$$= -e^{-1-\gamma} \sum_n \frac{\partial}{\partial(\alpha + \beta E_j)} e^{-n(\alpha + \beta E_j)}$$

$$= -e^{-1-\gamma} \frac{\partial}{\partial(\alpha + \beta E_j)} \left(\frac{1}{1 - \exp(-\alpha - \beta E_j)} \right)$$

$$= e^{-1-\gamma} e^{-\alpha - \beta E_j} \frac{1}{\{1 - \exp(-\alpha - \beta E_j)\}^2}$$

$$= \frac{\mathcal{N}_j}{\exp(\alpha + E_j/kT) - 1} \tag{8.52}$$

where, on the basis of thermodynamical reasoning[3] we have substituted $\beta = 1/kT$ in the last line of (8.52).

So far we have avoided any mention of the actual size of the cells τ_i. In classical mechanics, we can always assume that $\tau_i \to 0$, so that in the limit $n_i = N_i/\tau_i$ becomes the continuous phase-space density function $n(\mathbf{q}, \mathbf{p}) = \partial^2 N/\partial \mathbf{q}\, \partial \mathbf{p}$, q_i, p_i being the usual canonically conjugate position and momentum variables. In view of Heisenberg's uncertainty principle, (3.39), this simple approach is no longer possible, however, in quantum mechanics and it is necessary to find the minimum size of the cells τ_i. From (3.13) and (4.23) we find that for a particle in an infinitely deep potential well

$$p^2 = \hbar^2 k^2 = \frac{\hbar^2 \pi^2}{a^2}(l^2 + m^2 + n^2) = 2m_0 E_{lmn} \tag{8.53}$$

where, for simplicity, $a_x = a_y = a_z = a$, m_0 being the rest mass. From Fig. 4.3 we find that the smallest possible change in, say, p_x can be

obtained by putting $l+1$ in place of l; this alters the positive and negative value of k_x by π/a, so that the total change in the x component of the linear momentum of the particle is given by $\Delta p_x = \hbar\,\Delta k_x = \hbar 2\pi/a = h/a$. Since the same applies to the other two components we obtain

$$\Delta \mathbf{p} = \Delta p_x\,\Delta p_y\,\Delta p_z = \frac{h^3}{a^3} = \frac{h^3}{\Delta \mathbf{q}}$$

or

$$\tau_i = \Delta \mathbf{p}\,\Delta \mathbf{q} = h^3 \tag{8.54}$$

as another form of Heisenberg's uncertainty principle. But what we still require for our further calculations is Δp, where p is the magnitude of $\mathbf{p}$. To obtain this we treat (l, m, n) as three independent mutually perpendicular axes, bearing in mind that $p_x = \hbar k_x = \hbar\pi l/a$, etc.; (8.53) then gives us a triply infinite set of uniformly spaced points, as shown in Fig. 8.6. For
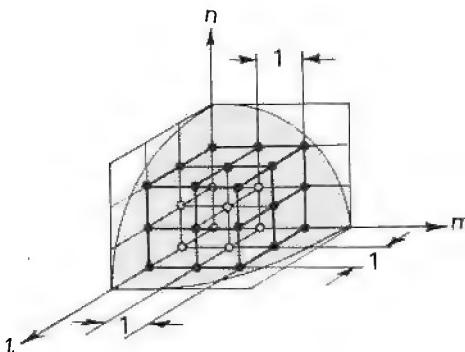
Fig. 8.6. Distribution of quantum states in a space constructed from the quantum numbers l, m, n.

large p the points corresponding to all states with the same magnitude of the linear momentum p_j approximately fall on the surface of a sphere of radius

$$R = \frac{p_j a}{\hbar\pi} = \frac{2p_j a}{h} \tag{8.55}$$

so that

$$\Delta R = \frac{2a}{h}\,\Delta p_j \tag{8.56}$$

Since only positive values of (l, m, n) are allowed, the volume of the relevant part of a shell corresponding to the interval $(p_j, p_j+\Delta p_j)$ is

given by

$$\frac{1}{8} 4\pi R^2 \,\Delta R = \frac{1}{8} 4\pi \frac{4p_j^2 a^2}{h^2} \frac{2a}{h} \Delta p_j$$

$$= \frac{4\pi p_j^2 a^3}{h^3} \Delta p_j \qquad (8.57)$$

Dividing both sides of (8.57) by $a^3 \,\Delta p_j$ we obtain the phase space density of the states,

$$Z_j(p) = \frac{4\pi p_j^2}{h^3} \qquad (8.58)$$

(It is possible to generalize these calculations to systems of arbitrary shape.)[4] In terms of the particle energy $E_j = p_j^2/2m_0$, where m_0 is the rest mass, we obtain, bearing in mind that $Z_j(p)\,\Delta p_j = Z_j(E)\,\Delta E_j$

$$Z_j(E) = \frac{2\pi}{h^3} (2m_0)^{\frac{3}{2}} E_j^{\frac{1}{2}} \qquad (8.59)$$

Since $Z_j(E)$ by definition gives the phase-space density of states (or cells τ_i) in a shell corresponding to the energy E_j, one can express it as $\mathcal{N}_j/\tau_j$, where from (8.42) $\mathcal{N}_j$ is the number of such cells and τ_j is their joint phase-space volume. Dividing both sides of (8.52) by τ_j and substituting for Z_j from (8.59), we obtain for the energy distribution of the particles

$$n_j = \frac{N_j}{\tau_j} = \frac{2\pi(2m_0)^{\frac{3}{2}} E_j^{\frac{1}{2}}}{h^3 \{\exp{(\alpha + E_j/kT)} - 1\}}$$

$$= \frac{\pi}{h^3} (2m_0)^{\frac{3}{2}} E_j^{\frac{1}{2}} \left\{ \coth \frac{1}{2} \left(\alpha + \frac{E_j}{kT} \right) - 1 \right\} \qquad (8.60)$$

the probability of a particle being found in the jth energy state being given by $P_j = n_j/N$, where N is their total number. Since $\sum_j n_j = n(\mathbf{q})$, where $n(\mathbf{q})$ is the volume density of the particles in ordinary space, in principle it is now possible to evaluate the constant α in terms of $n(\mathbf{q})$ and T, although it may not necessarily be the most convenient procedure to adopt, since α is quite a complicated function of the two parameters. In the classical limit, if $h \to 0$ and $\alpha \to \infty$ in such a way that $h^3 \exp \alpha \to C$, then, dividing both sides by $n(\mathbf{q})$, we obtain from (8.60), after normalization

$$f_j(E) = \frac{n_j}{n(\mathbf{q})} = \frac{2\pi}{n(\mathbf{q})C} (2m_0)^{\frac{3}{2}} E_j^{\frac{1}{2}} \, e^{-E_j/kT}$$

$$= \frac{2}{\pi^{\frac{1}{2}} k^{\frac{3}{2}} T^{\frac{3}{2}}} E_j^{\frac{1}{2}} \, e^{-E_j/kT} \qquad (8.61)$$

which is identical to (A5.19) of appendix 5.

A very important example of boson statistics is that of the quanta of electromagnetic radiation, i.e., photons. However, in the case of photons, we have to introduce the following changes in the derivation of (8.60). First of all, the number of photons does not remain constant, but may change due to interaction with matter. This means that the constraint (8.43) is no longer present and the corresponding Lagrange coefficient $\alpha = 0$. Secondly, since photons have zero rest mass, $m_0 = 0$, we find from (A1.8) of appendix 1 that their energy $E_j = p_j c$, $\Delta E_j = c \, \Delta p_j$, where c is the velocity of light. Thirdly, because of the two possible directions of polarization, each particle state corresponds to two photon states, so that (8.58) has an additional factor 2 on the right-hand side. Introducing the last two changes in (8.58) we obtain a new phase-space density of states

$$Z_j(E) = \frac{8\pi E_j^2}{h^3 c^3} \tag{8.62}$$

Substituting (8.62) in (8.52), dividing both sides by τ_j and putting $\alpha = 0$, we now obtain

$$n_j = \frac{8\pi}{h^3 c^3} \frac{E_j^2}{\exp(E_j/kT) - 1} \tag{8.63}$$

Multiplying both sides by $E_j = h\nu$, and changing the independent variable, we finally obtain Planck's expression for the density of black-body
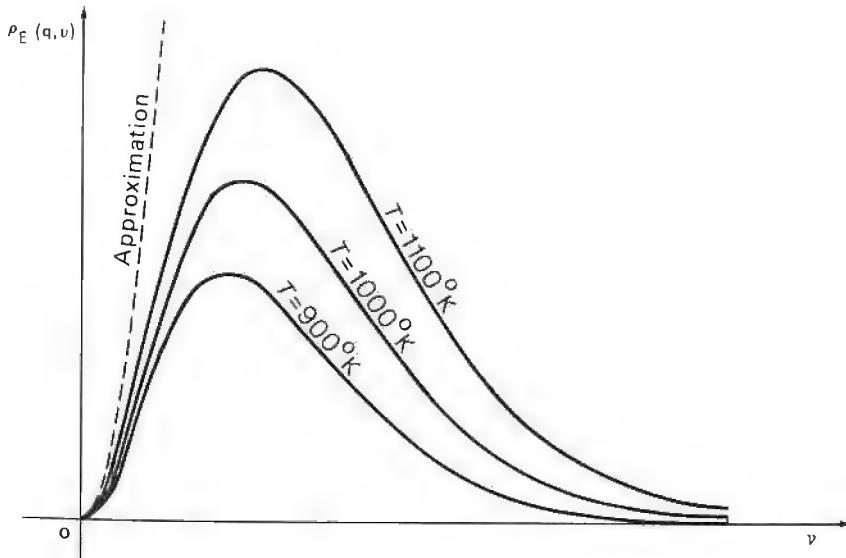
Fig. 8.7. Energy density of black-body radiation as a function of frequency.

radiation as a function of frequency

$$\rho_E(\mathbf{q}, \nu) = E_j n_j = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp(h\nu/kT) - 1} \tag{8.64}$$

We can now see that $\rho_E \rightarrow 0$ both for $\nu \rightarrow 0$ and $\nu \rightarrow \infty$ as was required to prevent the ultraviolet catastrophe[5] discussed in chapter 2. The dependence of ρ_E on ν is shown in Fig. 8.7, where the dotted line represents the same distribution for $T = 1100°K$ calculated on the basis of classical mechanics. The two agree at low frequencies but differ widely for large ν.

8.5. Fermi–Dirac statistics

After a somewhat heavy algebra of the last section it is a relief to find that the derivation of the Fermi–Dirac statistics is basically simpler. The main reason for this is the 'unfriendly' nature of particles characterized by antisymmetric wave functions, to which these particular statistics apply. It can be shown that such particles possess a half-integral spin, which enforces the antisymmetric properties of the wave functions.

We have seen in section 8.3 that when a system comprises several antisymmetric particles or fermions, they all have to be in different energy states. Thus now the summation (8.51) extends over two values only, $n = 0$ and 1.

$$\mathcal{N}_j = \sum_n \mathcal{N}_{nj} = \mathcal{N}_{0j} + \mathcal{N}_{1j}$$
$$= e^{-1-\gamma}\{1 + e^{-\alpha-\beta E_j}\} \tag{8.65}$$

Similarly, from (8.52), the number of particles N_j in each energy state is given by

$$N_j = \sum_n n\mathcal{N}_{nj} = \mathcal{N}_{1j} = e^{-1-\gamma} e^{-\alpha-\beta E_j}$$

$$= \frac{\mathcal{N}_j}{\exp(\alpha + \beta E_j) + 1} \tag{8.66}$$

Here again we find from thermodynamical reasoning that $\beta = 1/kT$. Since electrons are the most common particles following Fermi–Dirac statistics, it is convenient to use them as an example. We shall see in chapter 9 that the electron spin number $m_s = \pm\frac{1}{2}$, so that the right-hand side of (8.57) must be multiplied by a factor of two giving, in place of (8.59), the following expression for the phase-space density of states

$$Z_j(E) = \frac{4\pi}{h^3} (2m_0)^{\frac{3}{2}} E_j^{\frac{1}{2}} \tag{8.67}$$

Dividing both sides of (8.66) by τ_j and substituting (8.67) in (8.66), since

$Z_j = \mathcal{N}_j/\tau_j$ we obtain for the energy distribution of the electrons

$$n_j = \frac{N_j}{\tau_j} = \frac{4\pi(2m_0)^{\frac{3}{2}}E_j^{\frac{1}{2}}}{h^3\{\exp(E_j - E_F)/kT + 1\}}$$

$$= \frac{2\pi}{h^3}(2m_0)^{\frac{3}{2}}E_j^{\frac{1}{2}}\{1 + \tanh(E_j - E_F)/2kT\} \qquad (8.68)$$

where $\alpha = -E_F/kT$, and the probability of the Fermi level E_F being occupied is exactly equal to $\frac{1}{2}$. For large values of E_j, (8.68) becomes indistinguishable from the Boltzmann distribution, due to the relative smallness of the $+1$ term in the denominator. The Fermi–Dirac distribution is shown in Fig. 8.8 both for $T=0$ and $T>0$, where its relatively slight dependence on the temperature is clearly indicated. This explains the very low heat capacity of the electron gas in metals, since only those electrons with energies in the immediate vicinity of the Fermi level are
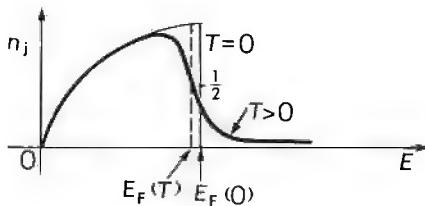
Fig. 8.8. Energy distribution based on Fermi–Dirac statistics.

free to acquire additional energy from heat; furthermore, due to atomic binding forces, only the outer shell electrons can contribute to the electron gas at all. This type of 'degenerate' gas is characterized by densities of the order 10^{20} particles per cm³. In its properties it differs radically from the electron gas commonly encountered in electron beams: the latter can be treated classically, its density being of the order of 10^{10} per cm³.[6]

Sections 8.4 and 8.5 of this chapter, together with appendix 5, can only provide a very brief introduction to the concepts of Boltzmann, Bose–Einstein, and Fermi–Dirac statistics. The three functions, $\{\exp E/kT + 1\}^{-1}$, $\exp(-E/kT)$ and $\{\exp E/kT - 1\}^{-1}$ are shown for comparison in Fig. 8.9; here the bracketed functions of (8.60) and (8.68) with $\alpha = E_F = 0$ are superimposed on the Boltzmann factor $\exp(-E/kT)$ of (A5.15) in appendix 5. We can clearly see that due to the peculiar collective properties of bosons and fermions the distributions markedly differ at very low values of E, although they become indistinguishable as the energy increases. These differences lead to new physical phenomena which occur at temperatures close to absolute zero. A fuller discussion of this can be found elsewhere.[7]
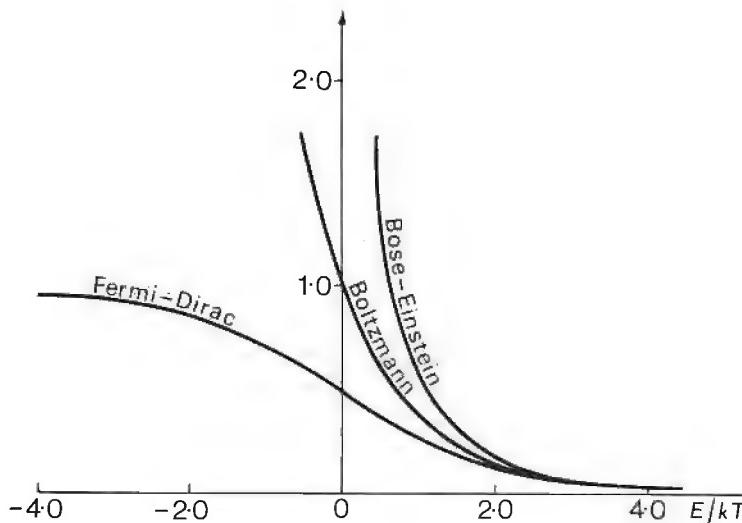
Fig. 8.9. Comparison of Bose–Einstein, Boltzmann, and Fermi–Dirac statistics.

Problems

1. How can we simplify the wave function Ψ of a system of N particles when the particles do not interact? Why?

2. Why is it that particles must be exactly the same for the exchange degeneracy to apply? What would happen if their masses were different, for example, by a very small amount, say 0·01 per cent? (Consider appendix 4.)

3. How general is the perturbation operator $\hat{H}'$ in (8.17)? Can you suggest forces which do not necessarily depend on $|z_2 - z_1|$?

4. Derive (8.29), (8.30) by substituting the two roots of the determinantal equation back in (8.20), (8.21). How does this differ from the degeneracy discussed in section 6.6?

5. Consider the probability density function $\Psi^*\Psi$ for symmetric and antisymmetric wave functions. Why do we talk about attractive and repulsive pseudoforces? Do these forces have any physical reality?

6. When the wave functions overlap we can no longer distinguish between separate trajectories of i different particles. Why is this so? How does it affect particle statistics in quantum mechanics?

7. Describe the difference between particle 'labelling' in classical and quantum mechanics (see appendix 5).

8. Use Stirling's formula (A5.3) for calculating $N!$ when $N = 2$ and $N = 8$.

9. Compare (8.45)–(8.48) with similar constraints in appendix 5. Why do we now have one more constraint?

10. Why do we have to invoke thermodynamical reasoning to calculate β? Does the expression for $\ln W$ remind you of something? Are you familiar with the concept of entropy $S = k \ln W$, where k is Boltzmann's constant?

11. Discuss (8.54); would it be possible to derive it directly from (3.39)? Why the difference in coefficients? Is it significant?

12. Plot (8.60) as a function of E_j; choose a plausible value for $\alpha > 0$. What happens near $E_j = 0$?

13. Calculate (8.64) as a function of the light wavelength, where, as usual $\lambda = c/v$. (Remember to substitute for both v and dv!) Where does the maximum now occur? Are you familiar with Wien's Law?

14. Discuss what happens when $T \rightarrow 0$ in (8.68). Where are all the electrons now? What is the probability of finding an electron with energy E_F? What would be the physical consequences of making $\alpha = +E_F$ instead of $-E_F$? Are you familiar with the concept of the Fermi sea of electrons in metals?

References

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9. Relativistic Wave Equation. Spin

So far we have been considering the non-relativistic Schrödinger equation only. In general, this is quite adequate in the case of particles moving with velocities $v \ll c$, where c is the velocity of light, but it fails to allow for the concept of spin which has to be introduced as an additional property for such particles as electrons and neutrons. It was Dirac's great achievement to present the laws of quantum mechanics in such a way that the idea of 'spin' became an integral part of the whole structure [1] instead of being a convenient expedient to account for the presence of additional energy levels. It should be noted however that some phenomena, e.g., Lamb shift, require a further development of Dirac's approach.

9.1. Experimental necessity for Dirac's approach

It was shown in (3.60a) that both time-dependent and time-independent Schrödinger equations can be constructed by substituting suitable expressions in the operator equation

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m_0} + \hat{V} \tag{9.1}$$

One can use the same procedure in constructing the relativistic Schrödinger equation although its validity must ultimately depend on experimental evidence. Since for a conservative system $\hat{H} = \hat{E}$, one can write, using (A1.3) of appendix 1, a relativistically correct expression for the kinetic energy of a particle as

$$(\hat{E} - \hat{V})^2 = c^2 \hat{\mathbf{p}}^2 + m_0^2 c^4 \tag{9.2}$$

(It can be shown from other relativity considerations that $\hat{V} = q\phi$ where q is electric charge and ϕ is electric potential [2]; it is further assumed that the vector potential $\mathbf{A} = 0$.) Substituting the correct expressions for the operators from (3.55), (3.57), and (3.59) and multiplying both sides of (9.2) by Ψ we obtain

$$-\hbar^2 \frac{\partial^2 \Psi}{\partial t^2} - 2Vj\hbar \frac{\partial \Psi}{\partial t} + V^2 \Psi = -c^2 \hbar^2 \nabla^2 \Psi + m_0^2 c^4 \Psi \tag{9.3}$$

where V is assumed to be independent of time. Writing

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\psi_t(t) \tag{9.4}$$

which is always permissible for a stationary state, and substituting (9.4) in (9.3) we obtain

$$\psi_t(t) = e^{-jEt/\hbar} \tag{9.5}$$

where E is again the separation constant. With the help of (9.5) the time-dependent Schrödinger equation (9.3) now reduces to

$$(-\hbar^2 c^2 \nabla^2 + m_0^2 c^4)\psi = (E - V)^2 \psi \tag{9.6}$$

which is a relativistically correct form for (4.17). Unfortunately, when (9.6) was applied to the hydrogen atom it gave an excessive correction for the fine structure energy levels of the electron.[3] This is due to the fact that (9.6) does not allow for 'spin' and can only be valid for spin-less particles, as in fact it is, whereas electrons possess spin and therefore require a different equation.

9.2. Dirac's wave equation

Dirac was the first to show how to obtain a relativistically correct wave equation for particles with spin.[4] Let us take (9.2) and solve it for E, using the positive sign of the square root only; substituting suitable expression for the operators $\hat{E}$, $\hat{V}$, and $\hat{p}$ and multiplying both sides of the equation by Ψ we obtain

$$j\hbar \frac{\partial \Psi}{\partial t} = (-c^2 \hbar^2 \nabla^2 + m_0^2 c^4)^{\frac{1}{2}}\Psi + V\Psi \tag{9.7}$$

Since there seems to be no way of attaching any physical significance to the square root of a Laplacian, not to mention the fact that (9.7) is asymmetrical with respect to space and time variables, Dirac decided that the expression under the square root sign must be a perfect square.[4] If it is, then it must be possible to write

$$\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 + m_0^2 c^2 = (\alpha_x \hat{p}_x + \alpha_y \hat{p}_y + \alpha_z \hat{p}_z + \beta m_0 c)^2 \tag{9.8}$$

The remarkable fact about (9.8) is that although we cannot satisfy it using scalar coefficients, we can if we use the following 4×4 matrices instead (see problem 2).

$$[\alpha_x] = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

$$[\alpha_y] = \begin{bmatrix} 0 & 0 & 0 & -j \\ 0 & 0 & j & 0 \\ 0 & -j & 0 & 0 \\ j & 0 & 0 & 0 \end{bmatrix}$$

$$[\alpha_z] = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

$$[\beta] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{9.9}$$

Of course this completely changes the nature of (9.7) since now instead of a scalar we have a matrix equation. Although we have used matrices in section 7.5, this was done for an entirely different purpose and at the time Dirac's approach was quite revolutionary. Substituting (9.9) in (9.7) we find that all the differential operators now become 4×4 matrix operators and follow the laws of matrix multiplication; the Ψ functions on the other hand become column matrices or spinors, as they are often called.

$$\Psi_i(\mathbf{r}, t) = \begin{bmatrix} \Psi_1(\mathbf{r}, t) \\ \Psi_2(\mathbf{r}, t) \\ \Psi_3(\mathbf{r}, t) \\ \Psi_4(\mathbf{r}, t) \end{bmatrix} \tag{9.10}$$

We can now write the following, relativistically correct wave equation in place of (9.7)

$$jh \frac{\partial}{\partial t} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} = \left\{ jch[\alpha_x] \frac{\partial}{\partial x} + jch[\alpha_y] \frac{\partial}{\partial y} + jch[\alpha_z] \frac{\partial}{\partial z} - m_0 c^2 [\beta] \right\} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} + V \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} \tag{9.11}$$

where it is customary to use the negative square root of (9.8). (Some authors use the positive square root, which seems tidier.[5]) Expressing each component of the column matrix $[\Psi_i(\mathbf{r}, t)]$ in (9.11) as a product of the type (9.4) we again obtain (9.5), so that

$$
\begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} e^{-jEt/\hbar} \tag{9.12}
$$

where E is the common separation constant. Substituting (9.12) back in (9.11) we finally obtain the Dirac wave equation

$$
jc\hbar \frac{\partial}{\partial x} \begin{bmatrix} \psi_4 \\ \psi_3 \\ \psi_2 \\ \psi_1 \end{bmatrix} + jc\hbar \frac{\partial}{\partial y} \begin{bmatrix} -j\psi_4 \\ j\psi_3 \\ -j\psi_2 \\ j\psi_1 \end{bmatrix} + jc\hbar \frac{\partial}{\partial z} \begin{bmatrix} \psi_3 \\ -\psi_4 \\ \psi_1 \\ -\psi_2 \end{bmatrix}
$$

$$
- m_0 c^2 \begin{bmatrix} \psi_1 \\ \psi_2 \\ -\psi_3 \\ -\psi_4 \end{bmatrix} = (E - V) \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \tag{9.13}
$$

Since two matrices are equal only when all their elements are equal, (9.13) corresponds to a set of four simultaneous, partial differential equations which have to be solved in place of, let us say (4.17), in order to obtain all the components of the energy eigenfunction $\psi(\mathbf{r})$. Often this is a formidable task and it is only fair to say that with Dirac's equation we have reached another degree of complexity in the solution of quantum mechanical problems.

9.3. Free particle in a one-dimensional world

In order to bring the salient features of Dirac's equation into focus let us consider the simplest possible case, namely, that of a free particle in a one-dimensional world. (The three-dimensional case is considered elsewhere.[6]) To make things easier we will assume that our wave packet, (3.19), has degenerated into a delta function in β (or k), so that although the linear momentum of the particle now has a precise value, we cannot say anything at all about its position. (This was the type of wave function originally considered by de Broglie.[7]) Since such a wave has a constant amplitude between $-\infty$ and $+\infty$, it is not physically realizable and therefore we cannot normalize it in the usual fashion. However, if such

a particle is contained in a very large box, the associated wave will approximate a pure sine wave very closely indeed, although it will contain a small admixture of sine waves of other frequencies. To avoid this and to retain the inherent simplicity of a pure sine wave we can use the so-called periodic boundary conditions, namely, we assume that the amplitude and slope of the wave function are (separately) equal at both ends of an interval, which is large compared to the wavelength λ. Since the integral of the square of the sine wave over such a finite interval will be finite, we can normalize it so that $\Psi^*\Psi$ dz again gives the probability of finding the particle in a given interval $(z, z+dz)$. As we shall see in chapter 10, periodic boundary conditions are widely used in the theory of solids both for one- and three-dimensional cases.

Since for a free particle $V=0$, (9.13) now reduces for a problem in one dimension to

$$jc\hbar \frac{\partial}{\partial z} \begin{bmatrix} \psi_3 \\ -\psi_4 \\ \psi_1 \\ -\psi_2 \end{bmatrix} - m_0 c^2 \begin{bmatrix} \psi_1 \\ \psi_2 \\ -\psi_3 \\ -\psi_4 \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \tag{9.14}$$

where we have assumed that the particle travels in the z-direction. But for a particle characterized by a precise momentum p (a δ-function wave packet), (3.19) can be rewritten as

$$[\Psi_i(z, t)] = [A_i] \, e^{-j(\omega t - \beta z)}$$
$$= [A_i] \, e^{j\beta z} \, e^{-jEt/\hbar} \tag{9.15}$$

where the constants A_i form a column matrix $[A_i]$. (Here β is a phase constant and must be distinguished from the matrix operator $[\beta]$.)

Substituting (9.15) in (9.14) and rearranging terms we obtain

$$\begin{bmatrix} E+m_0 c^2 & 0 & c\hbar\beta & 0 \\ 0 & E+m_0 c^2 & 0 & -c\hbar\beta \\ c\hbar\beta & 0 & E-m_0 c^2 & 0 \\ 0 & -c\hbar\beta & 0 & E-m_0 c^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{bmatrix} = 0 \tag{9.16}$$

Since (9.16) represents a homogeneous set of four algebraic equations, non-trivial solutions exist only when the determinant of its 4×4 matrix is equal to zero, i.e., when

$$(E^2 - m_0^2 c^4 - c^2 \hbar^2 \beta^2)^2 = 0 \tag{9.17}$$

Since $p=\hbar\beta$ (see (3.13)), this gives for the energy of the particle

$$E = \pm(c^2 p^2 + m_0^2 c^4)^{\frac{1}{2}} = E^{\pm} \tag{9.18}$$

in agreement with (9.2) and (A1.3) of appendix 1.

We now have the choice of taking either the positive or the negative sign in (9.18). The difference between quantum mechanics and classical mechanics is that, in classical mechanics, no physical significance can be attached to particles with negative E since there the lowest value of energy is $E = m_0 c^2$ (see (A1.1) of appendix 1), and $-m_0 c^2$ could only be reached by a discontinuous jump and not continuously, as is required. In quantum mechanics discontinuous jumps are permitted, however, and in fact the negative root of (9.18), namely E^-, gives physically significant solutions.[8] Experimental evidence shows that the positive sign of (9.18) can be identified with the case of electrons which have a negative electric charge, and the negative sign with positrons which have a positive electric charge. This duality or symmetry is characteristic of Dirac's equation and has considerable fundamental significance in quantum mechanics.

The form of (9.16) is such that we can only obtain two ratios of the coefficients A_i, namely, A_1/A_3 and A_2/A_4. For an electron using E^+, we obtain

$$\frac{A_1}{A_3} = -\frac{cp}{E^+ + m_0 c^2}$$

$$\frac{A_2}{A_4} = \frac{cp}{E^+ + m_0 c^2} \tag{9.19}$$

Since both roots of (9.17) are double, we can choose two arbitrary constants A_i for either solution. Making $A_4 = 0$ for the first solution and $A_3 = 0$ for the second we obtain from (9.15)

$$\Psi_\uparrow(z, t) = [\Psi_i(z, t)] = A_3 \begin{bmatrix} -d \\ 0 \\ 1 \\ 0 \end{bmatrix} e^{j(pz - E^+ t)/\hbar}$$

$$\Psi_\downarrow(z, t) = [\Psi_i(z, t)] = A_4 \begin{bmatrix} 0 \\ d \\ 0 \\ 1 \end{bmatrix} e^{j(pz - E^+ t)/\hbar} \tag{9.20}$$

where

$$d = \frac{cp}{E^+ + m_0 c^2} \tag{9.21}$$

(The meaning of the arrow subscript in (9.20) will be explained later.) In order to normalize the wave functions (9.20) over an interval $0 \leqslant z \leqslant l$,

we write, for example,

$$\int \Psi_\uparrow^* \Psi_\uparrow \, dz = A_3^* A_3 \begin{bmatrix} -d^* & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} -d \\ 0 \\ 1 \\ 0 \end{bmatrix} \int_0^l dz$$

$$= A_3^* A_3 (1 + d^* d)l$$

$$= A_3^* A_3 \frac{2E^+ l}{E^+ + m_0 c^2} = 1$$

so that

$$|A_3| = \left(\frac{E^+ + m_0 c^2}{2E^+ l} \right)^{\frac{1}{2}} \tag{9.22}$$

the phase remaining undetermined, as usual. Carrying out similar calculations for $\Psi_\downarrow$ (problem 7) we find that $|A_{4\downarrow}| = |A_{3\uparrow}|$. (When Ψ is a column matrix $[\Psi_i]$, its complex conjugate Ψ^* is the corresponding adjoint or row matrix $[\Psi_i]^\dagger = [\Psi_i^*]$.) It should be noted that, by making $A_3 = 0$ or $A_4 = 0$, we were able to obtain two solutions which are orthogonal (see problem 8); they represent what one would call in electrical engineering two normal modes. By definition no coupling exists between such modes, so that if one is excited it persists in the system without any tendency to excite the other mode. The same applies in quantum mechanics to eigenstates as we have mentioned before; if the electron is in a pure state associated with either of the eigenfunctions $\Psi_\uparrow$ or $\Psi_\downarrow$ it will remain so, as long as the system is not perturbed. However, as we have already seen in chapter 5, it is possible to assume that both states are excited simultaneously, the electron then being in a composite state, characterized by some linear combination of $\Psi_\uparrow$ and $\Psi_\downarrow$. This means that for any particular eigenvalue of p we now have the possibility of two eigenstates. These new states are associated with the electron spin, as we shall see shortly.

Let us now consider the algebraic form of $\Psi_\uparrow$ and $\Psi_\downarrow$ in more detail. In general, there is no easy way of presenting the wave functions $[\Psi_i]$ of (9.15) graphically, each component of the column matrix being a complex quantity. Even in the case of (9.20), when two components are zero, we still have no easy means of graphical representation, unless we agree to show the real and imaginary parts of each component separately. Then ψ_1 and ψ_3 or ψ_2 and ψ_4 can be represented as sine waves, one in the (z, x)- and the other in the (z, y)-plane, as shown, for example, in Fig. 9.1, for the function $\Psi_\uparrow$ (see problem 9 for $\Psi_\downarrow$).

The remarkable feature of Dirac's equation is that when the velocity of the particle $v \to 0$, the two solutions (9.20) still remain distinct. Thus

although (9.13) was originally derived for particles moving with relativistic velocities, its consequences persist even when the velocity of the particle $v=0$. But first let us consider what happens when $v \ll c$. Expressing (9.21) as a series we find that then

$$d = \frac{cp}{E^+ + m_0c^2} \approx \frac{cp}{2m_0c^2} = \frac{p}{2m_0c} = \frac{v}{2c} \ll 1 \qquad (9.23)$$

Thus, as v decreases, so does d, until for $v=0$ we have $d=0$, but since even then the non-zero components of $\Psi_\uparrow$ and $\Psi_\downarrow$ appear in different places, the two modes of (9.20) still remain distinct. This is only possible
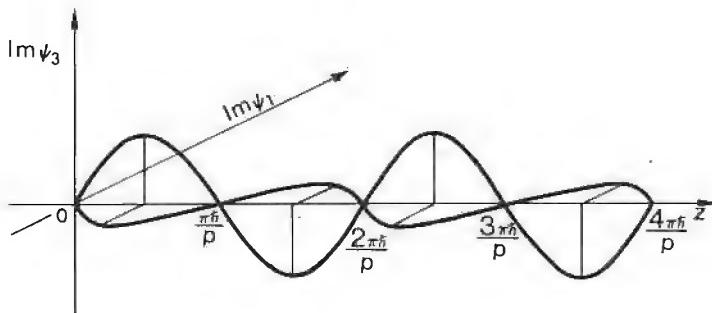
Fig. 9.1. The imaginary parts of the large and small components of the free electron wave function $\Psi_\uparrow$.

because now the wave functions $[\Psi_i]$ are no longer scalars but column matrices. Since for $v \ll c$ the d components of the matrix are very small, they can be neglected altogether for non-relativistic electrons and we obtain the following approximate expressions containing two-element column symbols only

$$\Psi_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix} A\, e^{j(pz - Et)/\hbar}$$

$$\Psi_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix} A\, e^{j(pz - Et)/\hbar} \qquad (9.24)$$

where from (9.22)

$$|A| = l^{-\frac{1}{2}} \qquad (9.25)$$

We may well ask now what would have happened to (9.20) if we had used the negative root E^- of (9.18). Substituting E^- in (9.16) we find that the new wave functions are very similar to those shown in (9.20), except that now the position of the large and small components is reversed. Such wave functions are taken to represent positrons rather than electrons.

9.4. Spin

Now that we are rather more familiar with Dirac's equation and the corresponding wave functions, let us consider some of its more general properties. We can rewrite (9.11) following Schiff,[9] in the following way

$$j\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{9.26}$$

where

$$\hat{H} = \hat{V} - c\hat{\alpha} \cdot \hat{\mathbf{p}} - \hat{\beta}m_0c^2 \tag{9.27}$$

and $\hat{\alpha} = (\hat{\alpha}_x, \hat{\alpha}_y, \hat{\alpha}_z)$. For simplicity, we have discarded the square brackets and the running subscripts of the matrices but retained their properties, so that (9.26) still represents a set of four simultaneous, partial differential equations. Assume that the potential energy V is not only due to an electrostatic field ϕ but also that it is spherically symmetrical, $\phi = \phi(r)$. We would then expect the orbital angular momentum of the particle to become a constant of motion. We can test this by noting that if a particle operator $\hat{O}$ is a constant of motion, it must commute with the corresponding Hamiltonian operator $\hat{H}$. Let us take the x component of the angular momentum operator $\hat{M}$—see (4.107)—and substitute in it (3.82) (see also [7.58]) by putting $\hat{O} = \hat{M}_x$. Now

$$j\hbar \frac{d\hat{M}_x}{dt} = [\hat{M}_x, \hat{H}]$$

$$= \hat{M}_x\hat{H} - \hat{H}\hat{M}_x \tag{9.28}$$

If the orbital angular momentum of the particle is, in fact, a constant of motion, then the right-hand side of (9.28) must be equal to zero. Substituting for $\hat{H}$ from (9.27), we obtain from the definition of $\hat{M}_x$, bearing in mind (3.69) and that both $\hat{V}$ and $\hat{\beta}$ commute with $\hat{H}$ (see also problem 10),

$$j\hbar \frac{d\hat{M}_x}{dt} = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)\hat{H} - \hat{H}(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)$$

$$= -c\{(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{\alpha}_x\hat{p}_x + \hat{\alpha}_y\hat{p}_y + \hat{\alpha}_z\hat{p}_z)$$

$$-(\hat{\alpha}_x\hat{p}_x + \hat{\alpha}_y\hat{p}_y + \hat{\alpha}_z\hat{p}_z)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)\}$$

$$= -c\{\hat{\alpha}_y[\hat{y}, \hat{p}_y]\hat{p}_z - \hat{\alpha}_z[\hat{z}, \hat{p}_z]\hat{p}_y\}$$

$$= j\hbar c\{\hat{\alpha}_z\hat{p}_y - \hat{\alpha}_y\hat{p}_z\}$$

$$= j\hbar c \begin{bmatrix} 0 & 0 & \hat{p}_y & j\hat{p}_z \\ 0 & 0 & -j\hat{p}_z & -\hat{p}_y \\ \hat{p}_y & j\hat{p}_z & 0 & 0 \\ -j\hat{p}_z & -\hat{p}_y & 0 & 0 \end{bmatrix} \tag{9.29}$$

Thus, due to the algebraic properties of $\hat{\alpha}$ matrices, the right-hand side of (9.29) clearly is not equal to zero and the angular orbital momentum **M** is not a constant of motion in this case. But, in view of the symmetry of the field, we would expect on purely physical grounds that there is a quantity associated with rotation which is conserved. Clearly, if we could find a set of matrices, one for each component of $\hat{\mathbf{M}}$, which, when added to $\hat{\mathbf{M}}$, make the sum commute with $\hat{H}$, we could solve the problem.

Let us consider the following set of matrices

$$\hat{M}_{sx} = \tfrac{1}{2}\hbar \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$\hat{M}_{sy} = \tfrac{1}{2}\hbar \begin{bmatrix} 0 & -j & 0 & 0 \\ j & 0 & 0 & 0 \\ 0 & 0 & 0 & -j \\ 0 & 0 & j & 0 \end{bmatrix}$$

$$\hat{M}_{sz} = \tfrac{1}{2}\hbar \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{9.30}$$

Substituting $\hat{M}_{sx}$ in (9.28), using (9.27) and bearing in mind the fact that $\hat{M}_{sx}$ commutes with $\hat{V}$, $\hat{\beta}$, and $\hat{\alpha}_x$, we now obtain

$$jh\, \frac{d\hat{M}_{sx}}{dt} = \hat{M}_{sx}\hat{H} - \hat{H}\hat{M}_{sx}$$

$$= -c\{\hat{M}_{sx}(\hat{\alpha}_x\hat{p}_x + \hat{\alpha}_y\hat{p}_y + \hat{\alpha}_z\hat{p}_z) - (\hat{\alpha}_x\hat{p}_x + \hat{\alpha}_y\hat{p}_y + \hat{\alpha}_z\hat{p}_z)\hat{M}_{sx}\}$$

$$= -c\{(\hat{M}_{sx}\hat{\alpha}_y - \hat{\alpha}_y\hat{M}_{sx})\hat{p}_y + (\hat{M}_{sx}\hat{\alpha}_z - \hat{\alpha}_z\hat{M}_{sx})\hat{p}_z\}$$

$$= -cjh\{\hat{\alpha}_z\hat{p}_y - \hat{\alpha}_y\hat{p}_z\}$$

$$= -jhc \begin{bmatrix} 0 & 0 & \hat{p}_y & j\hat{p}_z \\ 0 & 0 & -j\hat{p}_z & -\hat{p}_y \\ \hat{p}_y & j\hat{p}_z & 0 & 0 \\ -j\hat{p}_z & -\hat{p}_y & 0 & 0 \end{bmatrix} \tag{9.31}$$

which is exactly equal to (9.29) but with the sign reversed. Equation (9.31) clearly shows that, according to Dirac's equation, the quantity which

remains invariant in a spherically symmetric conservative system, e.g., in a hydrogen atom, is

$$\hat{\mathbf{M}}_j = \hat{\mathbf{M}}_l + \hat{\mathbf{M}}_s \tag{9.32}$$

i.e., the 'total' angular momentum of the particle and not just the orbital angular moment $\hat{\mathbf{M}} = \hat{\mathbf{M}}_l$, where we have used the subscript l for clarity.

The new matrix operator $\hat{\mathbf{M}}_s = (\hat{M}_{sx}, \hat{M}_{sy}, \hat{M}_{sz})$ is called the spin angular momentum of the particle.

When the particle velocity $v \ll c$, the spinors have only two, not four components, as shown in (9.24). The $\mathbf{\alpha}$ matrices then become the Pauli matrices

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad \hat{\sigma}_y = \begin{bmatrix} 0 & -j \\ j & 0 \end{bmatrix}, \qquad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{9.33}$$

and the momentum spin matrices reduce to

$$\hat{M}_{sx} = \tfrac{1}{2}\hbar\hat{\sigma}_x, \qquad \hat{M}_{sy} = \tfrac{1}{2}\hbar\hat{\sigma}_y, \qquad \hat{M}_{sz} = \tfrac{1}{2}\hbar\hat{\sigma}_z \tag{9.34}$$

The $\hat{\mathbf{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$ matrices defined in (9.33) were introduced by Pauli in his explanation of the details of electron energy levels in a hydrogen atom well before Dirac suggested his own, more general, solution of the problem. It is interesting to note that Pauli's matrices can be used as a short hand for writing the more general 4×4 matrices. For example, substituting (9.33) in (9.9) and (9.30) we obtain

$$\mathbf{\alpha} = \begin{bmatrix} 0 & \hat{\mathbf{\sigma}} \\ \hat{\mathbf{\sigma}} & 0 \end{bmatrix}, \qquad \hat{\beta} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}, \qquad \hat{\mathbf{M}}_s = \tfrac{1}{2}\hbar \begin{bmatrix} \hat{\mathbf{\sigma}} & 0 \\ 0 & \hat{\mathbf{\sigma}} \end{bmatrix} \tag{9.35}$$

where I is a 2×2 unit matrix. It should be noted that both the 4×4 and 2×2 $\hat{\mathbf{M}}_s$ matrices satisfy the same commutation relations as the angular momentum operator, (4.108). (See also problem 11.)

So far in our discussion of spin we have established that: (1) spin is an inherent property of some particles, e.g., electrons, since without it their angular momentum is not a constant of motion and (2) that the spin operator $\hat{\mathbf{M}}_s$ has the same commutation properties as the orbital angular momentum operator $\hat{\mathbf{M}}_l$, so that the two can be added together to give a new total angular momentum operator $\hat{\mathbf{M}}_j$, defined by (9.32). To complete the description it only now remains to calculate the eigenvalues and eigenvectors of the operator $\hat{\mathbf{M}}_s$.

We know that (4.67) and (4.110) together give an eigenvalue equation for $\hat{\mathbf{M}}_l^2$ of the type (3.65), namely,

$$\hat{\mathbf{M}}_l^2 \Psi = \mathbf{M}_l^2 \Psi = l(l+1)\hbar^2 \tag{9.36}$$

so that $l(l+1)\hbar^2$ are the eigenvalues of the orbital angular momentum

operator $\hat{\mathbf{M}}_l^2$, where $l=0, 1, 2,\ldots$ We could write this symbolically as

$$\mathbf{M}_l = \hbar\mathbf{l} \tag{9.37}$$

where the length of the vector $\mathbf{l}$ is not l but $\{l(l+1)\}^{\frac{1}{2}}$, as shown in (4.116) and Fig. 4.22. (Here we follow the notation of Siegman's book[10] which seems best for engineering applications.) Although these results were obtained with the help of the Schrödinger wave formulation of quantum mechanics, the same eigenvalues would have been obtained if we had used Heisenberg's matrix representation and diagonalized the corresponding matrix operator as explained in section 7.5 in connection with [7.48]–[7.50], the eigenvalues of the matrix being the eigenvalues of the corresponding operator and the eigenvectors representing the eigenfunctions. Let us now apply this procedure in the case of $\hat{\mathbf{M}}_s^2$, which is necessarily a matrix. Substituting from (9.34) we obtain

$$\hat{\mathbf{M}}_s^2 = \hat{M}_{sx}^2 + \hat{M}_{sy}^2 + \hat{M}_{sz}^2$$
$$= \tfrac{3}{4}\hbar^2\hat{\mathbf{\sigma}}^2$$
$$= \tfrac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{9.38}$$

Multiplying both sides of (9.38) by the two-element column matrix u we obtain the corresponding eigenvalue equation for the operator $\hat{\mathbf{M}}_s^2$

$$\hat{\mathbf{M}}_s^2 u = \mathbf{M}_s^2 u = s(s+1)\hbar^2 u \tag{9.39}$$

or

$$\tfrac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = s(s+1)\hbar^2 \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \tag{9.39}$$

where, for convenience, we have used a notation analogous to (9.36). Since the matrix is already in its diagonal form, we find that both eigenvalues of $\mathbf{M}_s^2$ are equal to

$$\mathbf{M}_s^2 = \tfrac{3}{4}\hbar^2 = \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2 \tag{9.40}$$

the corresponding eigenfunctions being given by two spinors

$$u_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \qquad u_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{9.41}$$

Since both eigenvalues are equal, we can represent the matrix $\mathbf{M}_s$ symbolically by a single vector $\mathbf{s}$, so that following (9.37),

$$\mathbf{M}_s = \hbar\mathbf{s} \tag{9.42}$$

Since $\hat{\mathbf{M}}_s$ appears jointly with $\hat{\mathbf{M}}_l$, the algebraic properties of Legendre

functions again require that the length of **s** must be $\{s(s+1)\}^{\frac{1}{2}}$ and not merely s. It is interesting to note that, using the commutation relations (4.108) rather than (4.107) for defining the angular momentum operator $\hat{\mathbf{M}}_s$, we have discovered the possibility of fractional angular momentum numbers s.

Let us now consider the z component of the angular momentum operators $\hat{\mathbf{M}}_l$ and $\hat{\mathbf{M}}_s$. Combining (4.66) and (4.109c) we obtain the following eigenvalue equation for the operator $\hat{M}_{lz}$

$$\hat{M}_{lz}\Psi = M_{lz}\Psi = m_l\hbar\Psi \tag{9.43}$$

where

$$M_{lz} = m_l\hbar \tag{9.44}$$

is treated as a projection of $\mathbf{M}_l$ on the z-axis, as shown in Fig. 4.22. In the case of the z component of $\hat{\mathbf{M}}_s$ we substitute the third of (9.34) in the general eigenvalue equation (3.65), and obtain

$$\hat{M}_{sz}u = M_{sz}u = m_s\hbar u \tag{9.45}$$

or

$$\tfrac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = m_s\hbar \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \tag{9.45}$$

which again is strongly reminiscent of (9.43). Since the matrix is diagonal, we find that the two eigenvalues are given by

$$M_{sz} = \pm\tfrac{1}{2}\hbar = m_s\hbar \tag{9.46}$$

the eigenfunctions u again being equal to the two spinors given by (9.41). The two values of M_{sz} are shown in Fig. 9.2, where M_{sz} is treated as a projection of the vector $\mathbf{M}_s$ on the z-axis, the whole procedure being similar to that of Fig. 4.22. This explains the notation of (9.24) where we have used the arrows to distinguish between the two different modes. The quantity m_s in (9.46) is called the spin quantum number and, in the case of an electron it has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$. Thus, when a particle has spin, it requires four rather than three quantum numbers for its full description. These quantum numbers can be either n, l, m_l, m_s (s being implied since it never varies for a given particle) or, possibly, n, l, j, m_j, whichever is more convenient, where j stands here for a quantum number obtained by a vector addition of l and s, and may have different values, although the magnitude of s is fixed, m_j being the projection of j on the z-axis. (An excellent discussion of this point which is of importance in the description of energy levels in materials suitable for maser applications can be found elsewhere.[10])

Since the spin angular momentum has all the characteristics of the orbital angular momentum, we would expect that a constant magnetic

field would cause the quantization of its z component M_{sz}, as was the case with the orbital angular momentum M_{lz}, (4.117)–(4.119) in section 4.8. This indeed is the case and it gives rise to the splitting of energy levels called the 'anomalous' Zeeman effect. The actual line separation corresponding to a given magnetic field will be discussed presently.
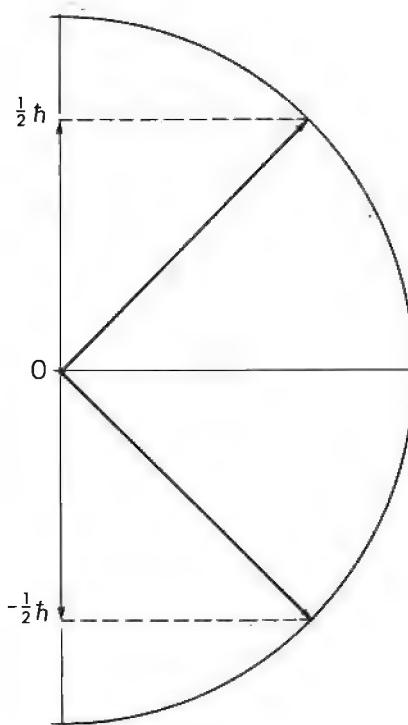
Fig. 9.2. Projections of the vector $\mathbf{M}_s$ representing the eigenvalues of the spin angular momentum operator $\hat{M}_{sz}$.

Let us consider the magnetic effects associated with the angular momentum of a charged particle. We have seen in section 4.8 that the ordinary Zeeman effect can be explained by assuming that an orbiting spin-less charged particle gives rise to a magnetic moment

$$\boldsymbol{\mu}_l = -\frac{e}{2m_0}\mathbf{M}_l = -\frac{e\hbar}{2m_0}\mathbf{l} \tag{9.47}$$

In the presence of a z-directed magnetic field the interaction energy is given by

$$E'_l = -\boldsymbol{\mu}_l\cdot\mathbf{B} = \frac{e\hbar}{2m_0}m_l\mathbf{B} \tag{9.48}$$

where m_l is the magnetic quantum number. Since, from Fig. 4.22, m_l can

have $(2l+1)$ different values, the same must apply to the interaction energy E_l'; this in turn leads to the $2l+1$ transitions shown in Fig. 4.23 and characteristic of the Zeeman effect. We shall show that Dirac's equation gives the correct value for the corresponding magnetic moment μ_s which is associated with the spin and which, surprisingly enough, cannot be obtained by merely substituting s for l in (9.47).

In order to calculate the effect of a magnetic field we must first of all incorporate it in the Hamiltonian operator $\hat{H}$ of (9.27). We know from classical mechanics and electron ballistics[11] that in the presence of a magnetic field $\mathbf{B}$, we must use $(\mathbf{p}+e\mathbf{A})$ in place of the linear momentum $\mathbf{p}$ in the Hamiltonian operator $\hat{H}$ where $\mathbf{A}$ is the vector potential defined by

$$\mathbf{B} = \text{curl } \mathbf{A} \qquad (9.49)$$

It can be shown that this representation is also relativistically correct[12] so that we can substitute directly in (9.26) and (9.27) to obtain

$$\{\hat{H}+e\hat{\phi}+c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})+\hat{\beta}m_0c^2\}\Psi = 0 \qquad (9.50)$$

Let us now premultiply both sides of (9.50) by the operator

$$\{\hat{H}+e\hat{\phi}-c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})-\hat{\beta}m_0c^2\}$$

This gives

$$\{(\hat{H}+e\hat{\phi})^2 - [c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})]^2 - \hat{\beta}^2 m_0^2 c^4 \\ + (\hat{H}+e\hat{\phi})c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}}) - c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})(\hat{H}+e\hat{\phi})\}\Psi = 0 \quad (9.51)$$

the remaining terms cancelling out, because the operator $\hat{\beta}m_0c^2$ commutes with the composite operators representing the other two terms. Since we are primarily interested in non-relativistic electrons, $v \ll c$, it is now convenient to simplify the algebra by introducing this condition in (9.51). Let us specify a new Hamiltonian operator $\hat{H}'$ which differs from the old Hamiltonian $\hat{H}$ by a constant,

$$\hat{H} = \hat{H}' + \hat{\beta}m_0c^2 \qquad (9.52)$$

so that

$$(\hat{H}+e\hat{\phi})^2 - \hat{\beta}^2 m_0^2 c^4 = (\hat{H}'+e\hat{\phi})^2 + 2m_0c^2\hat{\beta}(\hat{H}'+e\hat{\phi})$$

$$\approx 2m_0c^2\hat{\beta}(\hat{H}'+e\hat{\phi}) \qquad (9.53)$$

since, for $v \ll c$, both $\hat{H}'$ and $e\hat{\phi}$ are small compared with $\hat{\beta}m_0c^2$. Substituting this in (9.51) and dividing both sides of the equation by $2m_0c^2$ we obtain

$$\left\{(\hat{H}'+e\hat{\phi})\hat{\beta} - \frac{1}{2m_0}[\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})]^2 \right.$$

$$\left. + \frac{1}{2m_0c}[(\hat{H}+e\hat{\phi})\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}}) - \hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}}+e\hat{\mathbf{A}})(\hat{H}+e\hat{\phi})]\right\}\Psi = 0 \quad (9.54)$$

But the last two terms of (9.54) are smaller than the first two by a factor $1/c$ and again can be neglected in this approximation. Also, we know from (9.24) and (9.35) that, for the non-relativistic case, the wave function Ψ is a column matrix containing two rather than four terms, and the 4×4 $\hat{\boldsymbol{\alpha}}$ matrices must be replaced by the 2×2 $\hat{\boldsymbol{\sigma}}$ matrices. Introducing these changes in (9.54) we obtain

$$\left\{ (\hat{H}' + e\hat{\phi})I - \frac{1}{2m_0} \left[\hat{\boldsymbol{\sigma}} \cdot (\hat{\mathbf{p}} + e\hat{\mathbf{A}}) \right]^2 \right\} \Psi' = 0 \tag{9.55}$$

where I is a 2×2 unit matrix and $\Psi' = \Psi \exp(-jm_0 c^2 t/\hbar)$ and differs from Ψ only by a constant phase factor. Now the operational form of $\hat{H}'$ is again given by $j\hbar \, \partial/\partial t$ and (9.55) looks exactly like the Schrödinger equation except for the presence of the Pauli matrices $\hat{\boldsymbol{\sigma}}$. We may well suspect that this would be associated with some important physical difference, as indeed it is. In order to bring out this point, let us note that, in general, for two arbitrary vector operators $\hat{\mathbf{B}}$ and $\hat{\mathbf{C}}$ we have (see problem 12)

$$(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{B}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{C}}) = I(\hat{\mathbf{B}} \cdot \hat{\mathbf{C}}) + j\hat{\boldsymbol{\sigma}} \cdot (\hat{\mathbf{B}} \times \hat{\mathbf{C}}) \tag{9.56}$$

Using (9.56) to evaluate the last term of (9.55) we obtain

$$\begin{aligned}
[\hat{\boldsymbol{\sigma}} \cdot (\hat{\mathbf{p}} + e\hat{\mathbf{A}})]^2 &= I(\hat{\mathbf{p}} + e\hat{\mathbf{A}})^2 + j\hat{\boldsymbol{\sigma}} \cdot [(\hat{\mathbf{p}} + e\hat{\mathbf{A}}) \times (\hat{\mathbf{p}} + e\hat{\mathbf{A}})] \\
&= I(\mathbf{p} + e\hat{\mathbf{A}})^2 + je\hat{\boldsymbol{\sigma}} \cdot (\hat{\mathbf{p}} \times \hat{\mathbf{A}} + \hat{\mathbf{A}} \times \hat{\mathbf{p}}) \\
&= I(\hat{\mathbf{p}} + e\hat{\mathbf{A}})^2 + e\hbar \hat{\boldsymbol{\sigma}} \cdot \operatorname{curl} \mathbf{A}
\end{aligned} \tag{9.57}$$

where in the last line we have used relations of the form

$$\frac{A_y \partial \Psi}{\partial z} - \frac{\partial(A_y \Psi)}{\partial z} = -\frac{\Psi \partial A_y}{\partial z}$$

Substituting (9.57) in (9.45) and using (9.49) we now obtain

$$I\hat{H}'\Psi' = \left\{ -e\hat{\phi} + \frac{1}{2m_0} I(\hat{\mathbf{p}} + e\hat{\mathbf{A}})^2 + \frac{e\hbar}{2m_0} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{B}} \right\} \Psi' \tag{9.58}$$

Thus, in addition to the first two terms on the right-hand side which are exactly the same as the corresponding terms of the Schrödinger equation, we now have an additional term which represents the energy of interaction between the magnetic field $\mathbf{B}$ and the magnetic dipole due to the electron spin, $\boldsymbol{\mu}_s$. From the general expression (9.48) we can write in the case of a z-directed magnetic field for each mode

$$E'_s = -\boldsymbol{\mu}_s \cdot \mathbf{B} = \pm \frac{e\hbar}{2m_0} \mathbf{B} = \frac{e\hbar}{m_0} m_s \mathbf{B} \tag{9.59}$$

so that the magnetic moment associated with the spin is given by

$$\mu_s = -\frac{e\hbar}{m_0}\,\mathbf{s} \tag{9.60}$$

and, in terms of the quantum number s, is twice as large as the corresponding orbital magnetic moment μ_l, (9.47). This remarkable fact, which was amply confirmed by the experimental evidence of the anomalous Zeeman effect, was an outstanding achievement of Dirac's theory.

9.5. Electron in an infinitely deep potential well

In section 4.3 we discussed the stationary states of a particle contained in a rectangular, infinitely deep potential well, Fig. 9.3. Those calculations were correct as long as the particle had no spin and it is of some importance to repeat them now for a particle with spin $\frac{1}{2}$, e.g., an
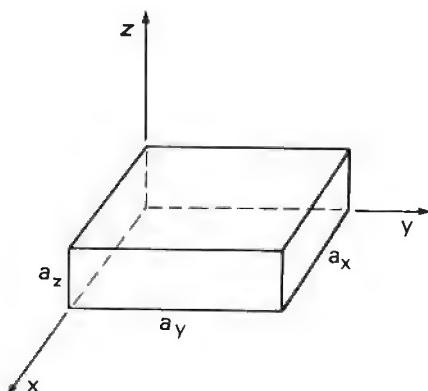
Fig. 9.3. A three-dimensional, rectangular potential well.

electron. Using Dirac's instead of Schrödinger's equation, where it is sufficient for our purpose to take the non-relativistic form (9.58), we obtain in the absence of the magnetic field, since $V = 0$ inside the potential well

$$\left\{ I\hat{H}' - \frac{1}{2m_0}\,I\hat{\mathbf{p}}^2 \right\}\Psi' = 0 \tag{9.61}$$

or, more explicitly

$$j\hbar\frac{\partial}{\partial t}\begin{bmatrix} \Psi'_1 \\ \Psi'_2 \end{bmatrix} = \frac{1}{2m_0}\begin{bmatrix} \hat{\mathbf{p}}^2 & 0 \\ 0 & \hat{\mathbf{p}}^2 \end{bmatrix}\begin{bmatrix} \Psi'_1 \\ \Psi'_2 \end{bmatrix} \tag{9.61}$$

This equation clearly shows that now each component of the wave function Ψ' must satisfy the equation, which is, in fact, the non-relativistic Schrödinger equation, but that the wave function still retains its matrix

form. Imposing the usual boundary conditions, (4.21), we can write the solution of [9.61] by inspection, using the spin eigenfunctions (9.41)

$$
\Psi_\uparrow' = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \psi_{lmn}\, e^{-jE_{lmn}t/\hbar}\, e^{-jm_0c^2t/\hbar}
$$

$$
= u_\uparrow \psi_{lmn}\, e^{-jE_{lmn}t/\hbar}\, e^{-jm_0c^2t/\hbar}
$$

$$
\Psi_\downarrow' = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \psi_{lmn}\, e^{-jE_{lmn}t/\hbar}\, e^{-jm_0c^2t/\hbar}
$$

$$
= u_\downarrow \psi_{lmn}\, e^{-jE_{lmn}t/\hbar}\, e^{-jm_0c^2t/\hbar} \tag{9.62}
$$

where ψ_{lmn} and E_{lmn} are respectively given by (4.22) and (4.23). The form of the two Ψ' functions is interesting because it not only shows the spinor form of the wave functions, but also that the energy eigenvalues of a particle in state l, m, n are $E_{lmn} + m_0c^2$ and not just E_{lmn}. Although this is strictly speaking true according to the theory of relativity, (A1.5) of appendix 1, it is customary in non-relativistic calculations to ignore this fact and we will do the same in the rest of this section substituting Ψ for Ψ'. Besides, the phase factor $\exp(-jm_0c^2t/\hbar)$ neither affects the value of the observables, since it disappears in the corresponding integrands, nor alters the spectrum, since the position of the lines depends on energy differences and not absolute values.

In order to acquire some familiarity with the new wave functions let us carry out one or two simple calculations. To begin with let us note that, the two spin eigenfunctions (9.41), are orthonormal, since, for example

$$
u_\uparrow^\dagger u_\uparrow = \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1 \tag{9.63}
$$

whereas

$$
u_\downarrow^\dagger u_\uparrow = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 0 \tag{9.64}
$$

Here the dagger superscript again indicates an adjoint matrix, i.e., the transpose of the complex conjugate of the original matrix (see also section 7.5). Using (9.63) and (9.64) we find, since by (4.22) the ψ_{lmn} functions form an orthonormal set, that

$$
\int \Psi_\uparrow^\dagger \Psi_\uparrow\, d\mathbf{r} = u_\uparrow^\dagger u_\uparrow \int \psi_{lmn}^* \psi_{lmn}\, d\mathbf{r} = 1 \tag{9.65}
$$

and

$$
\int \Psi_\downarrow^\dagger \Psi_\uparrow\, d\mathbf{r} = u_\downarrow^\dagger u_\uparrow \int \psi_{lmn}^* \psi_{lmn}\, d\mathbf{r} = 0 \tag{9.66}
$$

the same being true when the arrow signs are reversed in either equation. These calculations are based on the assumption that the spatial quantum numbers, l, m, n, remain the same, the two functions in (9.66) differing only in their spin quantum numbers indicated by the arrows.

Similarly, using $\Psi_\uparrow$ as an example, we can show that the mean energy of the quantum state l, m, n, is given by

$$\langle E \rangle = j\hbar \int \Psi_\uparrow^\dagger \frac{\partial}{\partial t} \Psi_\uparrow \, d\mathbf{r}$$

$$= j\hbar u_\uparrow^\dagger u_\uparrow \int \Psi_{lmn}^* \left(-\frac{j}{\hbar} E_{lmn} \right) \Psi_{lmn} \, d\mathbf{r}$$

$$= E_{lmn} \tag{9.67}$$

Since the same value is obtained using $\Psi_\downarrow$ and since in both cases E can be shown to have an exact value (see problem 14), this confirms the existence of eigenstates whose energy is independent of spin, in the absence of further interaction.

Finally, we can calculate the expectation value of the x component of the position and linear momentum of the electron. Substituting in the usual expressions for these quantities, we obtain

$$\langle x \rangle = \int \Psi_\uparrow^\dagger \hat{x} \Psi_\uparrow \, d\mathbf{r}$$

$$= u_\uparrow^\dagger u_\uparrow \int \psi_{lmn}^* x \psi_{lmn} \, d\mathbf{r}$$

$$= \tfrac{1}{2} a_x \tag{9.68}$$

and

$$\langle p_x \rangle = \int \Psi_\uparrow^\dagger \hat{p}_x \Psi_\uparrow \, d\mathbf{r}$$

$$= -u_\uparrow^\dagger u_\uparrow j\hbar \int \psi_{lmn}^* \frac{\partial}{\partial x} \psi_{lmn} \, d\mathbf{r}$$

$$= 0 \tag{9.69}$$

where the algebra and the results agree with those of (4.25) and (4.27). Thus, in the case of a single electron in a rectangular potential well the spin does not affect the value of the observables, although it increases the number of possible eigenstates and eigenfunctions by a factor of two.

9.6. Two electrons; Pauli's exclusion principle

Let us now consider the effect of spin on the exchange degeneracy discussed in section 8.3, assuming, for example, that we have two electrons in the same, one-dimensional, infinitely deep potential well.

Following [9.61] and (8.3), we find that the wave function Ψ of the system must satisfy the following differential equation

$$j\hbar \frac{\partial}{\partial t} \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} = \frac{1}{2m_0} \begin{bmatrix} p_{z1}^2 + p_{z2}^2 & 0 \\ 0 & p_{z1}^2 + p_{z2}^2 \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} \qquad (9.70)$$

Here Ψ is a function of two spatial variables z_1 and z_2, two spin variables s_1 and s_2 and time t, the spin being treated as an additional degree of freedom. For non-interacting particles and a stationary state, the wave function can be written as

$$\Psi(z_1, s_1, z_2, s_2, t) = \psi_\alpha(z_1, s_1)\psi_\beta(z_2, s_2)\psi_t(t) \qquad (9.71)$$

Substituting this in (9.70) we obtain (8.6) and the following two differential equations

$$\frac{d^2}{dz_1^2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \psi_{\alpha 1} \\ \psi_{\alpha 2} \end{bmatrix} + \frac{2m_0}{\hbar^2} E_\alpha \begin{bmatrix} \psi_{\alpha 1} \\ \psi_{\alpha 2} \end{bmatrix} = 0 \qquad (9.72)$$

$$\frac{d^2}{dz_2^2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \psi_{\beta 1} \\ \psi_{\beta 2} \end{bmatrix} + \frac{2m_0}{\hbar^2} E_\beta \begin{bmatrix} \psi_{\beta 1} \\ \psi_{\beta 2} \end{bmatrix} = 0 \qquad (9.73)$$

where

$$E = E_\alpha + E_\beta \qquad (9.74)$$

is the energy of the system, the values of E_α and E_β being respectively given by (8.12) and (8.13). Equation (9.74) shows that the energy of the system, E, is not altered when we interchange the particles. As we have already seen in section 8.3 this means that the system is exchange degenerate and the wave function must be a linear combination of the solutions of (9.72) and (9.73), as shown in (8.37), (8.38). Since the system is exchange degenerate for either z or s variables separately, the most general solution of (9.70) must have the form

$$\psi = \frac{1}{\sqrt{2}} \{\psi_\alpha(1)\psi_\beta(2) \pm \psi_\alpha(2)\psi_\beta(1)\} \frac{1}{\sqrt{2}} \{u_\uparrow(1)u_\downarrow(2) \pm u_\uparrow(2)u_\downarrow(1)\} \quad (9.75)$$

where the ψ functions are defined by (8.10) and (8.11) and the u functions are given by (9.41). The validity of (9.75) can be easily tested by substituting it back in (9.70) (see problem 15). However, experimental evidence shows that the electron wave functions must be antisymmetric, the sign of (9.75), for example, changing from plus to minus as we put 1 in place of 2 and vice versa. This is possible only when the two signs in brackets are opposite; this leads to two basically different types of solution:

$$\psi = \frac{1}{\sqrt{2}} \{\psi_\alpha(1)\psi_\beta(2) + \psi_\alpha(2)\psi_\beta(1)\} \frac{1}{\sqrt{2}} \{u_\uparrow(1)u_\downarrow(2) - u_\uparrow(2)u_\downarrow(1)\} \quad (9.76)$$

and

$$\psi = \frac{1}{\sqrt{2}}\{\psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)\}\frac{1}{\sqrt{2}}\{u_\uparrow(1)u_\downarrow(2) + u_\uparrow(2)u_\downarrow(1)\} \quad (9.77)$$

The first solution shows that if the spatial quantum number of the two particles is the same, their spin quantum numbers must be different, otherwise the wave function becomes identically equal to zero. This is an example of the well-known Pauli exclusion principle and our case applies to atomic electrons in an s-state, the state being characterized by a single quantum number n, the other two quantum numbers l and m_l being equal to zero. However, Pauli's principle covers electrons in other energy states as well and, in general, it is possible to say that all electrons in an atom must have different quantum numbers, including spin. If any two electrons happen to have the same spatial quantum numbers n, l, m_l, their fourth quantum number m_s must be different. This is an extremely important property of atomic electrons (see also section 8.5), and without it it is difficult to see how the properties of different chemical elements could have arisen.

In the case of solutions of the second type, (9.77), we must distinguish between three different arrangements of the spin eigenfunctions, all corresponding to the same spatial component,

$$\psi = \frac{1}{\sqrt{2}}\{\psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)\}u_\uparrow(1)u_\uparrow(2)$$

$$\psi = \frac{1}{\sqrt{2}}\{\psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)\}\frac{1}{\sqrt{2}}\{u_\uparrow(1)u_\downarrow(2) + u_\uparrow(2)u_\downarrow(1)\}$$

$$\psi = \frac{1}{\sqrt{2}}\{\psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)\}u_\downarrow(1)u_\downarrow(2) \qquad (9.77a)$$

The physical interpretation of these solutions requires careful consideration. Equations (9.77a) show that the wave function disappears when the spatial quantum number of the electrons is the same. Since the wave function is antisymmetric (it disappears if both quantum numbers of the two particles are the same), it follows that the solution applies only when the spin of both electrons is the same, their spatial quantum numbers being different. How is this possible in view of the fact that the second of (9.77a) contains spin eigenfunctions of either polarity? The explanation lies partly in the properties of the spin eigenfunctions and partly in the physical meaning that can be attached to observables in quantum mechanics.

We have already mentioned in connection with (9.32) that the orbital and spin angular momenta add vectorially. Dividing both sides of (9.32) by $\hbar$ we obtain, in fact,

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \qquad (9.78)$$

where the only possible values of the new quantum number j are

$$j = l+s, l+s-1, l+s-2, \ldots, |l-s| \tag{9.78a}$$

This property is based on the fact that the resultant vector operator $\hat{\mathbf{M}}_j$ must satisfy two eigenvalue equations of the type (9.39) and (9.45). Equation (9.78) can be extended to cover any number of particles; this leads to rather complicated expressions involving the so-called Clebsch–Gordon coefficients.[13] In the case of two electrons with $l_1 = l_2 = 0$ and spins $s_1 = s_2 = \frac{1}{2}$, see the first row in Fig. 9.4, we obtain, using (9.78) and (9.78a)

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \tag{9.79}$$

$$S = s_1 + s_2 = 1, \quad S = s_1 + s_2 - 1 = s_1 - s_2 = 0$$
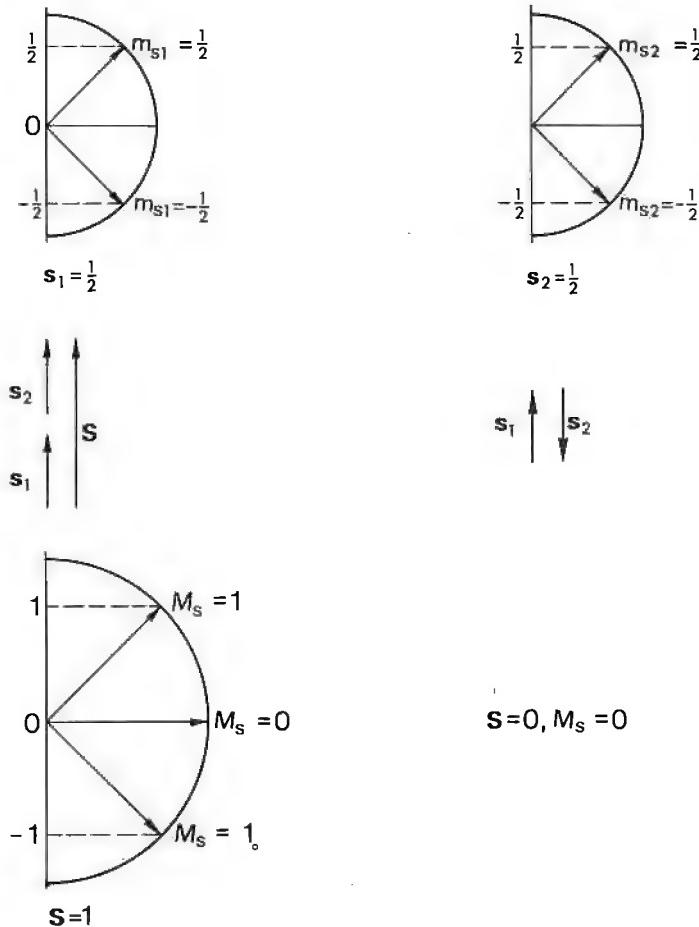
Fig. 9.4. Addition of spin vectors in a system comprising two electrons.

(It is usual in quantum mechanics to use lower case letters to represent the quantum numbers of individual particles and capitals for the corresponding quantum numbers of systems comprising several particles.) It is convenient to express (9.79) in the form of a vector diagram, as shown in the middle row of Fig. 9.4. However, if we place the system in a magnetic field, the direction of the vector S will be quantized in the usual manner, the three possible values of the spin quantum number of the system M_S being 1, 0, -1 for $S=1$ and zero for $S=0$, as shown in the bottom row of Fig. 9.4. The state for which $S=1$ is called a triplet since the corresponding energy splits into three separate levels under the influence of the magnetic field, the corresponding wave functions being given by (9.77a). Similarly, the state with $S=0$ is called a singlet, its energy being unaffected by the magnetic field, and its wave function being given by (9.76). The fact that the second of (9.77a) contains u functions of both polarities does not invalidate our argument because, as we have already seen in chapter 8, when two identical particles are in the same enclosure, i.e., when their wave functions overlap, all we can say is that they share two separate quantum states. It is only after the system has been split into two separate ones, each containing a single particle, that we can observe one particle in one energy state and the other particle in another. Therefore (9.76) and the second of (9.77a) mean that, in the first case, the two electrons share the two spin states in such a manner that the resultant spin of the system, when observed, is always zero, whereas in the second one, the two spins are shared in such a way that the resultant spin, when observed, is equal to one. There seems to be no difficulty in interpreting the first and third lines of (9.77a) since they indicate that then both electrons are permanently either in one or the other spin state.

Problems

1. Show, substituting suitable expressions for the operators, that (9.1) is equivalent to the time-dependent Schrödinger equation. What happens when we put $\hat{H} = \hat{E}$, which is valid for a conservative system?

2. Show that (9.8) can be satisfied if we use the matrices of (9.9) for the coefficients.

3. Write (9.11) in full and derive (9.13) by carrying out the matrix multiplications as indicated.

4. What happens when an electric transmission line is closed on itself? Can it then sustain oscillations at all frequencies? How does this compare with the periodic boundary conditions in quantum mechanics?

5. Write the equivalent of (9.14) and solve it when the particle is travelling in the x-direction. Has anything changed compared to the problem considered in the text?

6. Using E^-, which is the negative square root of (9.18), calculate the wave functions of a free positron. Compare the result with (9.20).

7. Calculate the normalizing constant A_4 for the wave function $\Psi_\uparrow$ assuming that the function is defined over an interval $0 \leqslant z \leqslant l$.

8. Show that the two functions $\Psi_\uparrow$ and $\Psi_\downarrow$ in (9.20) are orthogonal. Could you have obtained this result if the functions were scalars instead of column matrices?

9. Following Fig. 9.1 plot the real part of the two non-zero components of $\Psi_\uparrow$.

10. Derive the last line of (9.29) from (9.28) by making full use of the angular momentum commutation relations.

11. Substitute (9.33) and (9.34) in (4.108) and show that the 2×2 and 4×4 matrices satisfy the angular momentum commutation laws (they anti-commute).

12. Show that (9.56) is valid for two arbitrary vector operators $\hat{\mathbf{B}}$ and $\hat{\mathbf{C}}$.

13. Show that (9.65) and (9.66) will still be true when the arrow subscripts are reversed everywhere.

14. Calculate the mean energy $\langle E \rangle$ corresponding to (9.67) using the wave functions $\Psi_\uparrow$.

15. Show that (9.75) is a solution of (9.70).

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10. The Concept of Energy Bands in Crystals

The problems of solid state physics are often considered to be too specialized to justify inclusion in books on quantum mechanics. However, such an omission would seem to be unjustified in our case. Solid state devices play such an important role nowadays in electrical engineering that they are often responsible for a desire to learn quantum mechanics in the first place in order to understand their operation. For reasons of space we will discuss only one major problem of the solid state, namely, that of the so-called energy bands, and will use a periodically loaded electrical transmission line as an introductory model. Although there is no physical identity between this model and the corresponding quantum mechanical problem, the mathematical treatment is carefully chosen to be identical in both cases. This is possible because in both cases we have to consider wave propagation in periodic structures.

10.1. General description of the problem

In order to understand better the problem of energy levels in crystalline solids, the only type of solid of interest to us in this context, let us first consider some of their physical properties. Although different substances form crystals of vastly different shape, the distance separating individual atoms (nearest neighbours) is usually of the order of 3 Å, in some cases (e.g., caesium) becoming as much as 5 Å. Since the size of the corresponding atomic particles (electrons and neutrons) is of the order of 10^{-5} Å, the whole crystal largely consists of empty spaces permeated by various fields of force. In spite of this, even the smallest amount of material (e.g., a speck of dust) contains many atoms, a typical volume density being of the order of 10^{20} atoms per cm^3. Since the interaction between individual atoms can be both electrostatic (ionic and metallic bond), and quantum mechanical (covalent bond), the problem of energy levels in such a system is of immense complexity in its most general form. It is therefore necessary to introduce substantial simplifications before any useful solutions can be expected at all.

Broadly speaking, there are two different methods of approach. In the first method, due to Heitler and London,[1] use is made of the concept of 'weak coupling', a familiar idea to electrical engineers. It is assumed that

if the interaction between individual atoms is weak, we can first calculate the energy eigenvalues and the corresponding eigenfunctions of a single atom and then add the effect of the smoothed-out field of the remaining atoms as a perturbation, in a manner already discussed in chapter 6. Ionic crystals are particularly suitable for this type of approach, because there even the outermost electrons of an atom are relatively unaffected by the presence of other atoms in the lattice. In a somewhat loose sense one could say that in such crystals the electrons seldom venture away from their 'parent' atoms, so that the wave function of the whole system can be expressed to a good approximation in terms of the wave functions of individual atoms. This approach is quite helpful in considering the cohesive forces holding a crystal together, but it fails to provide us with an overall view of the crystal as a whole, since it ignores the individual existence of all atoms except one. Evidently, the Heitler–London approximation is not well suited for predicting those properties of crystals which are collective in nature and thus depend on the combined action of the coupling forces between many atoms, as is the case with electrical and thermal conduction in metals and semiconductors.

The second type of approximation originally developed by Hund, Mulliken, and Bloch[2] looks at the crystal from an entirely different point of view. Instead of concentrating on individual atoms, we consider the system as a whole and assume that the electrons do not 'belong' to individual atoms but are free to 'roam' in the crystal lattice. In this approximation, the presence of individual atoms and the spatial periodicity of the crystal lattice are represented by the periodic character of the corresponding potential function $V(\mathbf{r})$ appearing in the Schrödinger equation. The wave function of the system now consists of the wave functions of single electrons, each electron moving in a periodic field of force. The Bloch approximation, as it is often called for short, leads to the concept of energy bands, i.e., intervals determining the conduction properties of corresponding electrons. This is strongly reminiscent of some situations in the theory of electric filters, where, due to the complex pattern of internal coupling, the signal can be transmitted only over certain frequency bands. This type of approximation is particularly suitable for the discussion of conduction properties of crystals; 'allowed' and 'forbidden' energy bands play an important role in the description of the physical properties of semiconductors. In view of the great technological importance of these materials in present day electrical engineering, we will discuss the Bloch approximation and the corresponding energy bands in more detail.

10.2. Periodically loaded transmission line

Let us consider first of all a periodically loaded electric transmission line of characteristic impedance Z_0^0, as shown, for example, in Fig. 10.1,

the loading being in the form of series capacitors C_1. If the system is sufficiently long, i.e., if it contains a sufficiently large number of identical
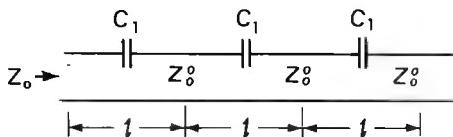
Fig. 10.1. Periodically loaded transmission line.

sections of the type shown in Fig. 10.2, its properties must approach those of another transmission line of a new characteristic impedance Z_0. We now wish to determine the voltage and current distribution of the new transmission line at different frequencies or, in other words, the functional relationship between the phase constant k^0 of the unloaded transmission line Z_0^0 and the phase constant k of the periodically loaded transmission line Z_0. (Here $k^0 = \omega(L^0 C^0)^{\frac{1}{2}} = \omega/v_p^0$ and $Z_0^0 = (L^0/C^0)^{\frac{1}{2}}$, where L^0 and C^0 are the inductance and capacitance per unit length of the unloaded line.)
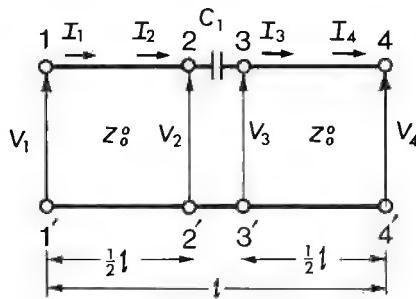
Fig. 10.2. Single section of a periodically loaded transmission line.

We can solve the problem in two different ways, the simpler one being treated first, the results in each case being expressed in the form of the ω–k diagram.

We know from the theory of transmission lines that, for the symmetrical section shown in Fig. 10.2, the following relationship must hold between (V_1, I_1) and (V_2, I_2), the subscripts 1 and 2 respectively referring to the terminals 1–1′ and 2–2′

$$V_1 = V_2 \cos \tfrac{1}{2} k^0 l + j Z_0^0 I_2 \sin \tfrac{1}{2} k^0 l$$

$$I_1 = j \frac{V_2}{Z_0^0} \sin \tfrac{1}{2} k^0 l + I_2 \cos \tfrac{1}{2} k^0 l \tag{10.1}$$

Assuming that the capacitors can be represented by an ideal, zero

length, section of the line we find from Fig. 10.2, that

$$V_2 = V_3 + Z_1 I_3$$

$$I_2 = I_3 \tag{10.2}$$

where $Z_1 = -j/\omega C_1$. Since the relationship between (V_3, I_3) and (V_4, I_4) is the same as that between (V_1, I_1) and (V_2, I_2), we can combine (10.1) and (10.2) and obtain, after successive substitutions,

$$V_1 = V_4 \left\{\cos k^0 l + j \frac{Z_1}{2Z_0^0} \sin k^0 l\right\}$$

$$+ j Z_0^0 I_4 \left\{\sin k^0 l - j \frac{Z_1}{2Z_0^0}(1 + \cos k^0 l)\right\}$$

$$I_1 = j \frac{V_4}{Z_0^0} \left\{\sin k^0 l + j \frac{Z_1}{2Z_0^0}(1 - \cos k^0 l)\right\}$$

$$+ I_4 \left\{\cos k^0 l + j \frac{Z_1}{2Z_0^0} \sin k^0 l\right\} \tag{10.3}$$

The same equation could have been obtained by applying the rules of matrix multiplication to the following expression

$$\begin{bmatrix} V_1 \\ I_1 \end{bmatrix} = \begin{bmatrix} \cos \frac{1}{2}k^0 l & j Z_0^0 \sin \frac{1}{2}k^0 l \\ \frac{j}{Z_0^0} \sin \frac{1}{2}k^0 l & \cos \frac{1}{2}k^0 l \end{bmatrix} \begin{bmatrix} 1 & Z_1 \\ 0 & 1 \end{bmatrix}$$

$$\times \begin{bmatrix} \cos \frac{1}{2}k^0 l & j Z_0^0 \sin \frac{1}{2}k^0 l \\ \frac{j}{Z_0^0} \sin \frac{1}{2}k^0 l & \cos \frac{1}{2}k^0 l \end{bmatrix} \begin{bmatrix} V_4 \\ I_4 \end{bmatrix} \tag{10.4}$$

Connecting in tandem a large number of the units shown in Fig. 10.2 we obtain a new transmission line of phase constant k and characteristic impedance Z_0. Now, the voltages and currents at both ends of a section of length l are given by

$$V_1 = V_4 \cos kl + j Z_0 I_4 \sin kl$$

$$I_1 = j \frac{V_4}{Z_0} \sin kl + I_4 \cos kl \tag{10.5}$$

Since (10.3) and (10.5) refer to the same system, the coefficients of I_4 and V_4 in the two equations must be equal. This gives three separate expressions, the most important of them being

$$\cos k^0 l + j \frac{Z_1}{2Z_0^0} \sin k^0 l = \cos kl \tag{10.6}$$

Equation (10.6) describes the so-called dispersion of the line, i.e., it gives the phase constant of the loaded line k as a function of k^0 or the angular frequency ω, where $k^0 = \omega/v_p^0 = 2\pi/\lambda^0$. In microwave engineering, such a dispersion chart is usually referred to as the 'ω–β' diagram, β being used in place of k. Such a diagram contains all the relevant information concerning wave propagation, since, for any $\omega = \omega(k)$, the phase velocity $v_p = \omega/k$ and the group velocity $v_g = d\omega/dk$ are readily available. If the system cannot transmit energy at certain frequencies, this will show as gaps or discontinuities in the corresponding ω–k diagram. For uniform transmission lines the ω–k diagram assumes the simple form of a straight line through the origin, the angle of the line with the k-axis being $\alpha = \tan^{-1}(1/v_p^0)$. The remaining two expressions obtained by equating appropriate coefficients of I_4 and V_4 in (10.3) and (10.5) give us, after eliminating Z_1, the ratio Z_0^0/Z_0 as a function of the angular frequency ω.

Before discussing the ω–k diagram of the transmission line shown in Fig. 10.1, let us rederive (10.5) using a method of approach which is quite general and, at the same time, more common in quantum mechanics than in electrical engineering. Figure 10.1 shows that the loaded transmission line is characterized by a constant admittance Y, and a variable impedance Z, the latter being equal to $jX^0 = j\omega L^0$ everywhere except at $z = (2n+1)\frac{1}{2}l$ when it discontinuously changes to $Z_1 = jX_1 = -j/\omega C_1$. Eliminating V between the transmission line equations

$$\frac{dV}{dz} = -ZI, \qquad \frac{dI}{dz} = -YV \tag{10.7}$$

we obtain

$$\frac{d^2I}{dz^2} = ZYI = f(z)I \tag{10.8}$$

where, now, the function $f(z) = ZY$ is periodic in z with period l. Linear differential equations with coefficients which are periodic functions have been studied in the past[3] and we know that their solutions must contain a periodic component. (For example, the solution of $dy/dx = (1 + \cot x)y$ is $y = e^x \sin x$, where both $1 + \cot x$ and $\sin x$ are periodic in x with period π, although the whole solution is not.) Floquet has shown[4] that in the case of (10.8) (Hill's equation), the solution must be of the form

$$I = c_1 e^{\mu z}u_1(z) + c_2 e^{-\mu z}u_2(z) \tag{10.9}$$

where u_1 and u_2 are periodic functions of z, their period being the same as that of $f(z)$. Depending on whether μ is real or imaginary, the coefficients $\exp(\pm \mu z)$ either signify growth (decay) or a change of phase; in the latter case the solution represents plane waves modulated in amplitude by the function $u(z)$. Contrary to what one might expect, the

main difficulty in the solution of the problem is invariably associated with the task of finding the right values for $\mu=\mu(\omega)$ rather than of defining the algebraic form of u_1 and u_2.

Let us now consider a trial solution of (10.8) of the form

$$I = e^{jkz}u(z) \tag{10.10}$$

where $\mu=jk$, in anticipation of the conditions prevailing in a pass-band. From (10.1) and Fig. 10.1 the following differential equation must be satisfied for each section of the uniform transmission line of characteristic impedance Z_0^0 and phase constant k^0

$$\frac{d^2I}{dz^2}+k^{02}I = 0 \tag{10.11}$$

Since the trial solution (10.10) must be valid everywhere, we can substitute it in (10.11) to obtain a differential equation for the function $u=u(z)$

$$\frac{d^2u}{dz^2}+2jk\frac{du}{dz}+(k^{02}-k^2)u = 0 \tag{10.12}$$

This is a linear differential equation with constant coefficients and the roots of its characteristic equation are

$$-jk\pm jk^0 \tag{10.13}$$

so that

$$u(z) = e^{-jkz}(A\cos k^0z+B\sin k^0z) \tag{10.14}$$

(Note that (10.14) when multiplied by $\exp jkz$ gives the usual solution of (10.11).)

In order to determine $k=k(\omega)$ we must consider the boundary conditions. Placing the origin at the point 2–2' in Fig. 10.2 we find that, since $u(z)$, by definition, must be periodic with period l,

$$u(0) = u(l) \tag{10.15}$$

$$-YZ_1u(0)+u'(0) = u'(l) \tag{10.16}$$

where primes signify differentiation with respect to z. Equation (10.16) was obtained by noting that a voltage drop $V=Z_1I$ across any one of the capacitors C_1 causes, according to (10.7), a discontinuous change $-YZ_1I$ in the slope of the current curve, Y being unaffected by the series loading. Substituting (10.14) in (10.15) and (10.16) we obtain

$$A = e^{-jkl}(A\cos k^0l+B\sin k^0l) \tag{10.17}$$

$$-YZ_1A-jkA+k^0B = -jke^{-jkl}(A\cos k^0l+B\sin k^0l)$$
$$+k^0e^{-jkl}(-A\sin k^0l+B\cos k^0l) \tag{10.18}$$

These equations are homogeneous, their solution being non-trivial only when the determinant

$$\begin{vmatrix} 1-e^{-jkl}\cos k^0 l & -e^{-jkl}\sin k^0 l \\ -YZ_1-jk+e^{-jkl} & k^0+e^{-jkl} \\ \times(jk\cos k^0 l+k^0\sin k^0 l) & \times(jk\sin k^0 l-k^0\cos k^0 l) \end{vmatrix} = 0 \quad (10.19)$$

After some manipulation (see problem 3) we again obtain

$$\cos k^0 l+j\frac{Z_1}{2Z_0^0}\sin k^0 l = \cos kl \quad (10.6)$$

(In going from (10.19) to (10.6) we have used the identity $Y/k^0=j/Z_0^0$ which is generally valid for uniform, loss-less transmission lines.) Having derived (10.6) twice let us consider its physical significance. To make this task easier we note that by putting $Z_1=-j/\omega C_1$ we obtain

$$j\frac{Z_1}{2Z_0^0} = \frac{1}{2\omega C_1 Z_0^0} = \frac{l}{2v_p^0 C_1 Z_0^0}\cdot\frac{1}{k^0 l} = \frac{\pi}{k^0 l} \quad (10.20)$$

π being chosen as the arbitrary constant for convenience. Substituting in (10.6) we now obtain

$$\cos k^0 l+\frac{\pi}{k^0 l}\sin k^0 l = \cos kl \quad (10.21)$$

The left-hand side of (10.21) is shown in Fig. 10.3 as a function of $k^0 l$. With the help of this figure and (10.21) we finally obtain Fig. 10.4 which gives $k^0 l$ as a function of kl, the required ω–k diagram for the periodic transmission line shown in Fig. 10.1.

Let us now discuss (10.21) and the corresponding Figs. 10.3 and 10.4
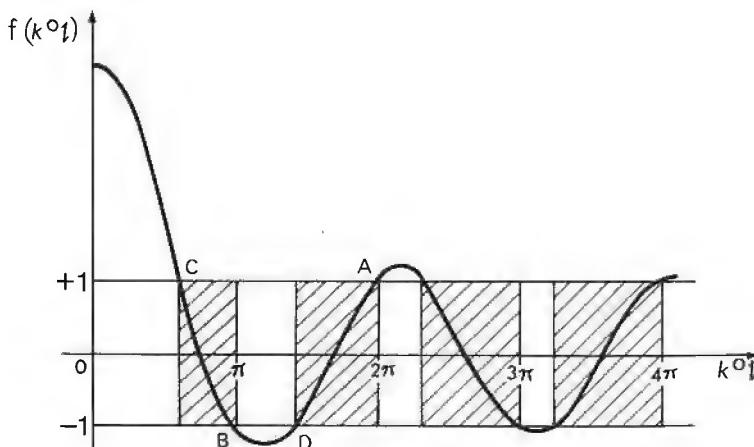
Fig. 10.3. The left-hand side of (10.21) as a function of $k^0 l$.

in some detail. First of all we note that real solutions of (10.21) can only exist when $|\cos kl| < 1$, i.e., when the left-hand side of (10.21) lies in the interval $(-1, 1)$. For all other values of ω (and hence k^0) the solutions kl become imaginary and lead to hyperbolic functions of the type $\cos kl = \cos j\alpha l = \cosh \alpha l$, the travelling wave of (10.1) now becoming an exponentially decaying disturbance, characterized by an attenuation co-efficient α. Equation (10.21) clearly shows that, in general, a periodically loaded transmission line acts as an electric bandpass filter, transmitting signals at some frequencies and attenuating them at others. When the
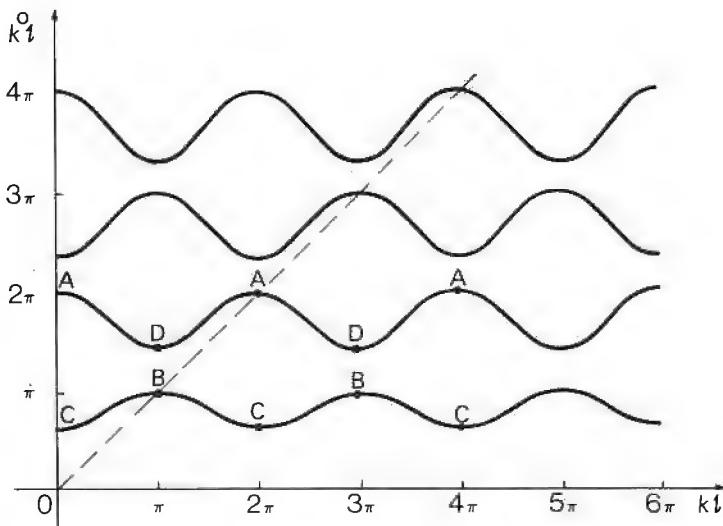
Fig. 10.4. ω–k diagram of a periodically loaded transmission line.

left-hand side of (10.21) is exactly equal to ± 1, the transmission line supports a perfect standing wave, which consists of two waves of equal amplitude and travelling in opposite directions. The wave travelling to-wards the terminal load is set up by the generator connected across the input of the line, whereas the wave travelling in the opposite direction is due to reflexions from the loading capacitors C_1, each capacitor constituting a discontinuity in the characteristic impedance Z_0^0 of the uniform line. In this case no energy is transmitted along the line, although a considerable amount of energy is stored in it, as is usual in the case of resonant circuits. When the left-hand side of (10.21) is less than 1 but greater than -1, the wave travelling from the generator towards the terminal load has a greater amplitude than the sum of the reflections travelling in the opposite direction. Thus we now have a net flow of energy between the generator and the load, the line acting as a filter operating in its pass-band. Finally, when the frequency is such that the

left-hand side of (10.21) is greater than $+1$, or less than -1, the reflections caused by the capacitor C_1 heavily outweigh the effect of the wave attempting to travel from the generator to the load. Now, after a brief transient, the wave-like character of the current voltage along the line is destroyed and we are left with a decaying field which remains in phase everywhere and is pulsating at the frequency of the signal generator.

Two observations should be made at this point. So far, we have assumed that the line is infinitely long or that it is terminated by a matched load. In practice, such an assumption could not be satisfied at all frequencies, so that (10.21), Fig. 10.3, and the ω–k diagram of Fig. 10.4 are only approximately true. Whenever the effect of the terminating load becomes noticeable, we get new values of k which are not contained in the ω–k diagram of Fig. 10.4. These new solutions are of great importance in the case of crystals, where they are called the 'surface states'. In general, it is quite difficult to calculate the conditions on a periodically loaded transmission line of finite length and it is usually more convenient to assume that the line is closed on itself. This leads to the so-called 'periodic boundary conditions', which eliminate all changes in the ω–k diagram of Fig. 10.4, due to the proximity of the load; at the same time, they cause a break-up of the continuous curves into a series of points, since a closed circuit can only support an integral number of half-wavelengths of current or voltage. However, for a large number of sections the dotted curves become virtually indistinguishable from the continuous curves.
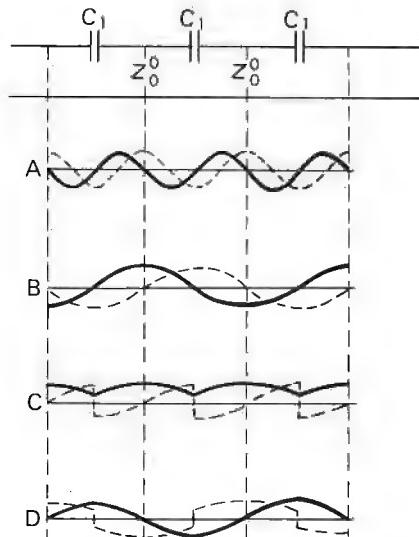
Fig. 10.5. Voltage (- - - - -) and current (———) distribution on a periodically loaded transmission line.

Finally, we find from Fig. 10.4 that the curves repeat exactly every 2π in the kl direction. This is simply due to the fact that, in the presence of loading, the current and voltage curves may have a complicated shape, which substantially differs from a simple sine wave (see Fig. 10.5). Such complex waves can be thought to consist of an infinite number of spatial or Hartree harmonics, the phase constant of the nth harmonic being given by $k_n = k_0 + 2\pi n$. Thus, the repetitions in the direction of the horizontal axis of Fig. 10.4 correspond to different spatial harmonics of the composite wave. Since Fig. 10.4 contains information concerning the phase constants only, it cannot tell us anything about the relative amplitudes of the component waves, the latter depending on the parameters of a given transmission line.

10.3. Kronig–Penney model of a one-dimensional, crystal lattice

Having investigated the distribution of current and voltage in a periodically loaded transmission line, let us now consider the model of a one-dimensional crystal lattice, originally proposed by Kronig and Penney.[5] Figure 10.6 shows the appropriate potential distribution which is assumed to have the form of a periodic δ-function, $V(z)$ being zero everywhere except at points l apart where it tends to infinity in such a
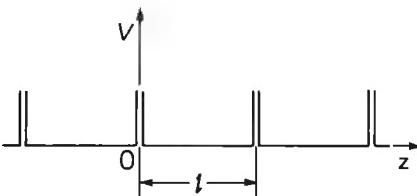
Fig. 10.6. Kronig–Penney model of a one-dimensional crystal lattice.

way that $\int V(z)\,dz$ remains finite and equal to a constant C. (A somewhat different model with infinitely deep wells in place of infinitely high potential barriers is discussed elsewhere.)[6]

Inside the crystal the electron wave function must satisfy the usual wave equation

$$\frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}\{E - V(z)\}\psi = 0 \tag{10.22}$$

where the potential function $V(z)$ is now periodic with period l. According to Floquet's theorem,[4] the solutions of (10.22) must have the form

$$\psi = e^{jkz}u(z) \tag{10.23}$$

where $u(z)$ is again periodic with period l. However, between the atoms

$V(z)=0$ and (10.22) reduces to

$$\frac{d^2\psi}{dz^2} + k^{02}\psi = 0 \tag{10.24}$$

where

$$k^{02} = \frac{2mE}{\hbar^2} \tag{10.25}$$

Substituting (10.23) in (10.24) we obtain

$$\frac{d^2u}{dz^2} + 2jk\frac{du}{dz} + (k^{02} - k^2)u = 0 \tag{10.26}$$

which is identical to (10.12). By analogy, its solution can be written as

$$u(z) = e^{-jkz}(A \cos k^0z + B \sin k^0z) \tag{10.27}$$

where k^0 is now given by (10.25) and represents the phase constant of a free electron of energy E. In order to find the phase constant k of the wave function ψ inside the crystal and express it as a function of k^0 or E, the latter being more usual, we use the periodic boundary conditions which have to be satisfied by the function u. Since u and du/dz must be continuous at both ends of the interval of length l, we obtain

$$u(0) = u(l) \tag{10.28}$$

In order to calculate the change of slope u' across the infinitely thin barriers representing atoms, we write (10.22) in the form of finite differences

$$\Delta \text{ (slope of } \psi) = -\frac{2m}{\hbar^2}\{E - V(z)\}\psi \, \Delta z \tag{10.29}$$

As $\Delta z \to 0$ straddling the barrier, $E \, \Delta z \to 0$ but $V(z) \, \Delta z \to C$, so that the change in slope of the function ψ is given by

$$\psi'(0_+) - \psi'(0_-) = \frac{2m}{\hbar^2} C\psi(0) \tag{10.30}$$

Substituting (10.23) in (10.30) we obtain

$$jk \, e^{jkz}u(0) + e^{jkz}u'(0_+) - jk \, e^{jkz}u(0) - e^{jkz}u'(0_-) = \frac{2m}{\hbar^2} C \, e^{jkz}u(0) \tag{10.31}$$

which immediately simplifies to

$$u'(0_+) - u'(0_-) = \frac{2m}{\hbar^2} Cu(0) \tag{10.32}$$

Choosing $0_+ = 0$, $0_- = l$, we obtain from (10.32)

$$u'(0) = u'(l) + \frac{2m}{\hbar^2} C u(0) \tag{10.33}$$

the slope u' now being the same at the beginning of each interval. Substituting (10.27) in (10.28) and (10.32) we obtain a determinantal equation identical to (10.19), except for $(2m/\hbar^2)C$ in place of YZ_1. By analogy to (10.6) and (10.21) we can write

$$\cos k^0 l + \frac{mC}{\hbar^2 k^0} \sin k^0 l = \cos kl \tag{10.34}$$

the corresponding k^0–k diagram being shown in Fig. 10.4. In the case of a periodically loaded transmission line, k^0 was proportional to the angular frequency ω, but in the present case k^0 is related to the kinetic energy of free electrons, E, (10.25), and in quantum mechanics it is more usual to represent (10.34) in the form of an E–k diagram, as shown in Fig. 10.7. Now, in the absence of a periodic field, the straight line $k^0 = k$, of Fig. 10.4, becomes a parabola $E = \hbar^2 k^2 / 2m$, in agreement with Fig. 3.3.

Several questions now arise in connection with Fig. 10.7. We have already stated that for $C \to 0$, i.e., for a vanishingly small atomic field, Fig. 10.7 must degenerate to a parabola. This is possible only if we choose
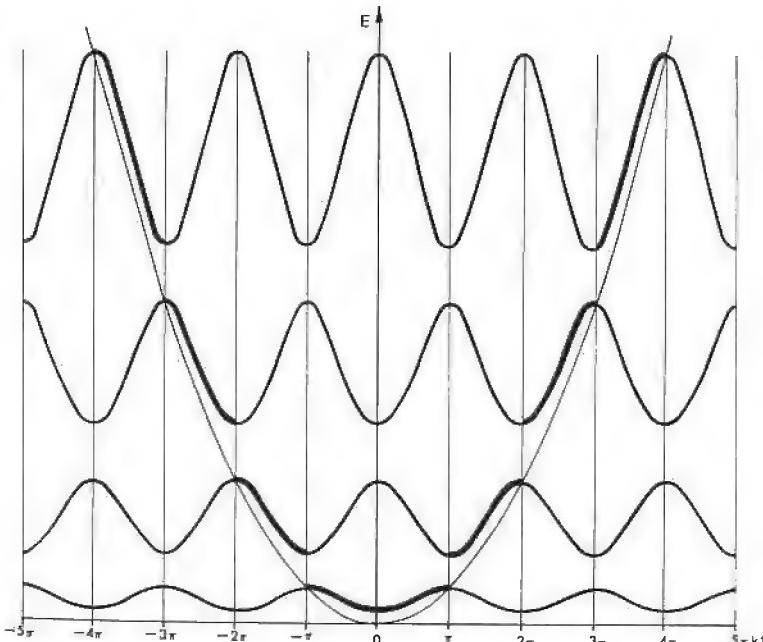
Fig. 10.7. E–k diagram for a one-dimensional crystal lattice.

one particular branch of each $E = E(k)$ curve, as shown by the thick line in Fig. 10.7. What does the periodicity in the k-direction signify, however? It seems that no physical meaning can be attached to it; by (10.27) the periodicity represents a phase shift of $\exp j2n\pi$, n being an integer and, as we know, such phase shifts cancel out whenever we calculate $\psi^*\psi$ which, as the probability density function, enters into all physically significant calculations. It is therefore customary in quantum mechanics to consider only one strip ($kl = 2\pi$ or $k = 2\pi/l$ wide) for each energy band. Figure 10.7 can then be drawn more concisely in the form of Fig. 10.8, where all the thick-line sections have been transferred to a single interval $-\pi/l \leqslant k \leqslant \pi/l$.
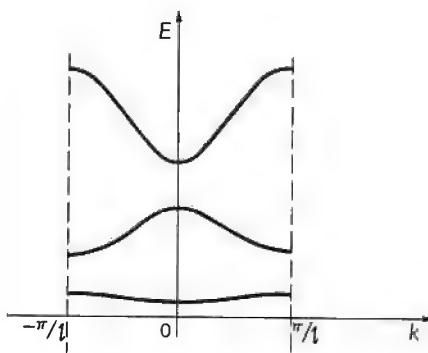
Fig. 10.8. Reduced zone representation of an E–k diagram.

Another question one could ask in connection with Figs. 10.7 and 10.8 is: why does the width of the pass-bands vary as we move along the E-axis? Since E represents the kinetic energy of the electrons, we would expect the force exerted by individual atoms to appear relatively strong for small E, in the limit the bands degenerating into single energy states, valid for completely isolated electrons. On the other hand, for high energy electrons the pass-bands must be relatively wide, the electrons being affected only slightly by the atoms. In the limit, the corresponding E–k curves degenerate into a continuous, free electron parabola. Let us now consider the stop bands. For the wave functions corresponding to these energies the reflections from the first few atoms of the lattice reinforce so strongly that the lattice becomes quite impenetrable to such electrons. We find from Figs. 10.4 and 10.7 that one edge of each stop band is given by the condition $k^0 l = n\pi$, n being an integer. Putting $k^0 = 2\pi/\lambda$ we can write this in the form

$$n\lambda = 2l$$

which can be recognized as Bragg's condition for a complete reflection of incident radiation of wavelength λ by a crystal lattice of periodicity l.

The so-called 'dynamic theory of diffraction' extends this simple approach somewhat further and directly leads to the concept of stop bands, in complete agreement with Fig. 10.7. It may be added that the edges of the stop bands correspond to perfect standing waves which are respectively symmetric and antisymmetric in character, as was the case in a periodically loaded transmission line, Fig. 10.5, the I and ψ functions being identical in the two cases. Since the electron charge distribution is given by $-e\psi^*\psi$, it will be different in the two cases leading to different energies E inside the crystal for the same value of k. This is reminiscent of the two kinds of resonance encountered at both edges of the stop-band of a periodically loaded transmission line, which occur at different frequencies ω and correspond to different amounts of electromagnetic energy stored in the line.

Finally, let us consider the behaviour inside the lattice of an electron whose energy falls within one of the pass-bands of Figs. 10.7 or 10.8. If no external forces are present the wave function (10.23) satisfies the energy eigenvalue equation (10.22) and the electron, following (3.47), will move with the group velocity $v_g = \mathrm{d}E/\hbar\,\mathrm{d}k$, experiencing neither acceleration nor retardation, as long as the crystal lattice is perfectly periodic. Although, in principle, this would suggest a completely free passage of electrons through the crystal lattice, crystal defects and impurities would never allow it in practice. Let us now assume that a small electric field is applied across the crystal. Under the influence of the field the electron acquires energy and gradually moves across the energy band, k increasing under the influence of the force (see (3.50)), until it reaches the top of the band, when its mean velocity becomes zero. Since the edge of the band corresponds to Bragg's condition for total reflection, the positive and negative values of the electron velocity must be equally probable, so that the mean velocity becomes zero, in agreement with the zero slope of the E–k curve. (Since (10.23) does not satisfy the linear momentum eigenvalue equation, the velocity and linear momentum of the electron are not well-defined, the wave function being in the form of a wave packet.) Under the continued influence of the external field the electron velocity changes sign and becomes negative, until the electron reaches the other edge of the band, when the mean velocity becomes positive again. (When the external field is very strong, the electron may jump across an energy gap separating two pass-bands.)[7] Thus, ideally, under the influence of an external field, the electron does not move across the lattice, but oscillates about its mean position. However again, in practice, crystal imperfections and impurities will invariably interrupt this cycle, setting up a steady drift velocity across the crystal. This observation suggests that although the present analysis was quite successful in predicting the existence of energy bands, it requires further amplification for a detailed analysis of transport phenomena.[8]

10.4. Three-dimensional crystal lattices—Brillouin zones

The solutions (10.23) of the Schrödinger equation (10.22) describing the conditions in a one-dimensional lattice are identical to the current functions I of section 10.2 and are shown for four values of ω (or E) in Fig. 10.5. Since the constituent $u(z)$ functions, (10.14) and (10.27), are periodic with period l, we can express them in the form of Fourier series

$$
\begin{aligned}
u(z) &= \sum_n c_n\, e^{j2\pi nz/l} \\
&= \sum_n c_n\, e^{j2\pi nbz} \\
&= \sum_n c_n\, e^{jnkz}
\end{aligned}
\tag{10.35}
$$

the limits of summation being $(-\infty, +\infty)$ throughout. Here $b = 1/l$ is the reciprocal of the period l and $k = 2\pi/l$ is the phase constant of the fundamental. As the distance l over which the wave repeats itself increases, the phase change per unit length k decreases and so does the fundamental unit along the k-axis in Fig. 10.8.

In crystallography, it is usual to call the collection of points occupied by the atoms in Fig. 10.6 the direct lattice, l being the identity period of the lattice, i.e., the smallest possible translation which transforms the lattice into itself. Similarly, the corresponding points of the b-axis form the so-called reciprocal lattice, $1/l$ being its identity period. Lastly, the horizontal axis of Fig. 10.8 given by $k = 2\pi b$, is referred to as the k-space, the $(-\pi/l, +\pi/l)$ or $(-\pi b, +\pi b)$ interval being called the reduced zone.
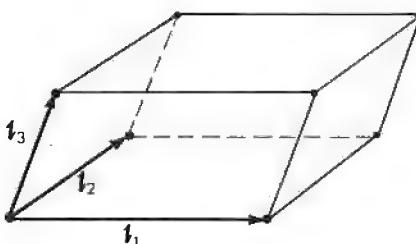
Fig. 10.9. A three-dimensional crystal lattice.

These terms acquire their full significance when applied to three-dimensional lattices, as we shall see in a moment. In general, an idealized crystal lattice contains an ordered, three-dimensional array of points, each point corresponding to the position of a single atom, as shown for example in Fig. 10.9. Bloch[9] has shown that then the function u of (10.23) is again periodic, but with a periodicity in three dimensions corresponding to the unit cell of the direct crystal lattice. Since now $u = u(\mathbf{r})$ where

$\mathbf{r} = (x, y, z)$ is the position vector, it can be represented by a triple Fourier series

$$u(\mathbf{r}) = \sum_{\mathbf{n}} \mathbf{c_n}\, e^{j(2\pi\mathbf{n}/l)\mathbf{r}}$$

$$= \sum_{\mathbf{n}} \mathbf{c_n}\, e^{j2\pi(\mathbf{n}\cdot\mathbf{b})\mathbf{r}}$$

$$= \sum_{\mathbf{n}} \mathbf{c_n}\, e^{j(\mathbf{n}\cdot\mathbf{k})\mathbf{r}} \tag{10.36}$$

Here $\mathbf{n} = (n_1, n_2, n_3)$ is a vector whose components are all integers and $\mathbf{l} = (\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ is the identity period of the direct lattice shown in Fig. 10.9, a translation $\mathbf{l}$ transforming the crystal into itself. What meaning can we now attach to the reciprocal lattice and its identity vector $\mathbf{b} = (\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ corresponding to the inverse distance $b = 1/l$ of the one-dimensional problem? First of all we note that, by definition, $u(\mathbf{r} + \mathbf{l}) = u(\mathbf{r})$. Substituting this in the second of (10.36) we find that, in order to obtain integral values for $(\mathbf{n}\cdot\mathbf{b})$ required by the periodicity condition in the three directions $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$, we must have

$$\begin{aligned} \mathbf{b}_i\mathbf{l}_j &= 1 \quad \text{if} \quad i = j \\ &= 0 \quad \text{if} \quad i \neq j \end{aligned} \tag{10.37}$$

According to (10.37) vector $\mathbf{b}_1$ of the reciprocal lattice, for example, must be perpendicular to vectors $\mathbf{l}_2$ and $\mathbf{l}_3$ of the direct lattice, which in turn define a plane. In other words

$$\mathbf{b}_1 = c(\mathbf{l}_2 \times \mathbf{l}_3) \tag{10.38}$$

c being an undetermined scalar multiplier. However, since $\mathbf{l}_1 \cdot \mathbf{b}_1 = 1$ by definition, we have

$$b_1 = \frac{1}{l_1 \cos \theta_1} \tag{10.39}$$

θ_1 being the angle between the vectors $\mathbf{b}_1$ and $\mathbf{l}_1$. Substituting (10.39) in (10.38) we obtain

$$\frac{1}{c} = \frac{|\mathbf{l}_2 \times \mathbf{l}_3|}{b_1} = l_1 \cos \theta_1 |\mathbf{l}_2 \times \mathbf{l}_3| = \mathbf{l}_1 \cdot (\mathbf{l}_2 \times \mathbf{l}_3)$$

so that (10.38) can finally be written

$$\mathbf{b}_1 = \frac{\mathbf{l}_2 \times \mathbf{l}_3}{\mathbf{l}_1 \cdot (\mathbf{l}_2 \times \mathbf{l}_3)} \tag{10.40}$$

By cyclically changing the subscripts 1, 2, and 3 we obtain from (10.40) suitable expressions for the remaining two component vectors $\mathbf{b}_2$ and

$\mathbf{b}_3$. The wave vector $\mathbf{k} = (\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ can now be obtained by simple multiplication

$$\mathbf{k}_1 = 2\pi\mathbf{b}_1$$
$$\mathbf{k}_2 = 2\pi\mathbf{b}_2 \qquad\qquad (10.41)$$
$$\mathbf{k}_3 = 2\pi\mathbf{b}_3$$

This equation is the three-dimensional equivalent of the simple definition of the phase constant $k = 2\pi b = 2\pi/l$.

Having discussed the E–k diagrams for one-dimensional problems in some detail we are now in a position to describe their extension to three dimensions, although, for reasons of space, we do not propose to solve any three-dimensional problems. In the one-dimensional case the electron energy E is a function of a single variable k, as shown, for example, in Figs. 10.7 and 10.8. In a three-dimensional case the electron energy E, in general, is a function of three independent variables $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$, or k_x, k_y, k_z if we choose cartesian coordinates. It is difficult to represent E as a function of three independent variables graphically, although one can always draw surfaces representing constant values of E; alternatively, one could fill the k-space with a coloured substance, the value of E at a given point k being indicated by the intensity of the dye. We would then discover that the dye intensity exhibits certain well defined discontinuities which form closed surfaces corresponding to the $k = \pm n\pi$ points of the one-dimensional problem. These surfaces enclose the so-called Brillouin zones, each zone corresponding to a different $kl = 2\pi$ interval along the k-axis of Fig. 10.7. All Brillouin zones have the same k-space volume, although topologically they tend to be very complicated; their position plays a fundamental role in the discussion of energy bands in a three-dimensional crystal. In order to simplify the problem of representation of the $E(\mathbf{k})$ function we might choose to plot it along a preferred direction such as a diagonal or an edge of the reciprocal lattice. The plot of E as a function of $\mathbf{k}$ along several such directions would then give us some basic features of the three-dimensional dependence of E on $\mathbf{k}$. This method of representation is frequently used when E depends on $\mathbf{k}$ in a complicated fashion, as it does, for example, in the crystals of silicon and germanium.

It should be fairly clear from this brief summary that the construction of E–k diagrams for three-dimensional crystals is a task of some complexity, in particular, since it often leads to totally new configurations such as, for example, band overlapping, which cannot occur in the case of a one-dimensional lattice. However, the problem is of great importance in the discussion of the properties of solids and great efforts are being made to obtain as much information as possible over a wide range of technologically significant materials.

Problems

1. Discuss the physical nature of the solid state when viewed microscopically.

2. Is (10.6) an exact equation ? If not, why not ? What are the assumptions behind the validity of (10.5) ?

3. Solve (10.19) and show that it reduces to (10.6).

4. The functions I in Fig. 10.5 are the same as the wave functions ψ in the Kronig–Penney model of a crystal lattice. Can you suggest the shape of the ψ functions if we use infinitely thin potential wells in place of potential barriers? Is the electron then more likely to be inside the potential well or outside it?

5. Explain in your own words why the edge of a pass-band corresponds to the electron energy associated with Bragg reflection?

6. Show that (10.23) does not satisfy the eigenvalue equation for the linear momentum $-j\hbar \, d\Psi/dx = p\Psi$. Does this surprise you ? Is a particle subjected to a periodic field of force a free particle ?

7. Using (10.40) plot the reciprocal lattice of a cube and a parallelepiped. What happens when you change the period size of the direct lattice ?

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9. F. Bloch, op. cit. (see Ref. 2).

Appendix 1.
Relativity Correction

If a free particle travels with a velocity approaching that of light, $v \sim c$, (3.7) and (3.8) are no longer valid, the energy of the particle of rest mass m_0 now being given by[1]

$$E = mc^2 = \frac{m_0 c^2}{(1 - v^2/c^2)^{\frac{1}{2}}}$$

$$\approx m_0 c^2 + \tfrac{1}{2} m_0 v^2 + \cdots \qquad (A1.1)$$

Since the linear momentum of the particle is

$$p = \frac{m_0 v}{(1 - v^2/c^2)^{\frac{1}{2}}}$$

$$\approx m_0 v + \cdots \qquad (A1.2)$$

we obtain, substituting in (A1.1)

$$E^2 = c^2 p^2 + m_0^2 c^4 \qquad (A1.3)$$

Since (3.9) is still valid we obtain, substituting it in (A1.1) and, at the same time, making use of (3.13), which is equally valid for relativistic and non-relativistic systems[2]

$$\hbar^2 \omega^2 = c^2 p^2 + m_0^2 c^4$$

$$= c^2 \hbar^2 \beta^2 + m_0^2 c^4 \qquad (A1.4)$$

or

$$\omega = \left(c^2 \beta^2 + \frac{m_0^2 c^4}{\hbar^2} \right)^{\frac{1}{2}} \qquad (A1.5)$$

Equation (A1.5) represents a hyperbola with the asymptotes

$$\omega = \pm c\beta \qquad (A1.6)$$

as shown in Fig. A1.1. This curve corresponds to the parabola of Fig. 3.3, but differs from it in one important respect; its slope, i.e., the group velocity $v_g = d\omega/d\beta$ can never exceed the velocity of light c, as is consistent with (A1.1) and (A1.2). Also, from the definition of the phase

velocity v_p and bearing in mind that (A1.1) and (A1.2) give $E = pc^2/v$, where $v = v_g$, we can readily obtain

$$v_p = \frac{\omega}{\beta} = \frac{\omega\hbar}{p} = \frac{E}{p} = \frac{c^2}{v_g} \tag{A1.7}$$

Electrical engineers will recognize (A1.7) as the relationship between phase and group velocities in an unloaded waveguide. In fact, the validity of this expression is much more general.[3]
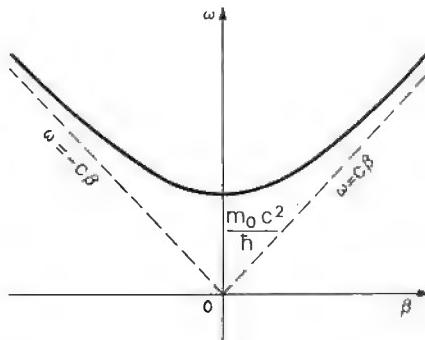
Fig. A1.1. $\omega = \omega(\beta)$ curve for a free, relativistic particle.

For photons the rest mass $m_0 = 0$ and their energy

$$E = pc \tag{A1.8}$$

the velocity of travel v being equal to c. Indeed, we find from (A1.2) that, in the circumstances, this is necessary in order to keep the linear momentum p different from zero.

References

1. H. Goldstein, op. cit.; Chapter 6.
2. L. de Broglie, op. cit.
3. R. W. Ditchburn, Phase-velocity and group-velocity in relativistic optics, *Revue Optique* **27**: 4–14 (1948). J. L. Synge, Phase-velocity and group-velocity in relativistic optics, *Revue Optique* **31**: 121–2 (1952).

Appendix 2.
Poisson Brackets in Classical Mechanics

Consider a function of seven independent variables $\mathbf{q}$, $\mathbf{p}$, and t. Its total derivative with respect to time is given by[1]

$$\frac{du}{dt} = \sum_i \left(\frac{\partial u}{\partial q_i} \dot{q}_i + \frac{\partial u}{\partial p_i} \dot{p}_i \right) + \frac{\partial u}{\partial t}$$

$$= \sum_i \left(\frac{\partial u}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial H}{\partial q_i} \right) + \frac{\partial u}{\partial t}$$

$$= [u, H] + \frac{\partial u}{\partial t} \tag{A2.1}$$

where we have used Hamilton's canonical equations of motion

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = -\frac{\partial H}{\partial p_i} \tag{A2.2}$$

to obtain the so-called Poisson brackets, which are defined in general as

$$[u, v] = \sum_i \left(\frac{\partial u}{\partial q_i} \frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial q_i} \right) \tag{A2.3}$$

q_i, p_i being the canonical coordinates, i.e., the coordinates appearing in Hamilton's canonical equations of motion (A2.2). Putting $u = q_i$ or $u = p_i$ in (A2.1) we can now write (A2.2) in terms of Poisson's brackets

$$\dot{p}_i = [p_i, H], \quad \dot{q}_i = [q_i, H] \tag{A2.4}$$

Putting $u = H$ in (A2.1) we obtain the usual identity

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} \tag{A2.5}$$

Finally, if u does not contain time explicitly, $u = u(\mathbf{q}, \mathbf{p})$, then

$$\frac{du}{dt} = [u, H] \tag{A2.6}$$

Further, if $[u, H] = 0$, then u becomes a constant of motion.

Finally, from the definition of Poisson's brackets we obtain the following important relationships which apply to the canonically conjugate coordinates q_i, p_i:

$$[q_i, q_j] = \sum_k \left(\frac{\partial q_i}{\partial q_k} \frac{\partial q_j}{\partial p_k} - \frac{\partial q_i}{\partial p_k} \frac{\partial q_j}{\partial q_k} \right) = 0 \qquad (A2.7)$$

$$[p_i, p_j] = \sum_k \left(\frac{\partial p_i}{\partial q_k} \frac{\partial p_j}{\partial p_k} - \frac{\partial p_i}{\partial p_k} \frac{\partial p_j}{\partial q_k} \right) = 0 \qquad (A2.8)$$

$$[q_i, p_j] = \sum_k \left(\frac{\partial q_i}{\partial q_k} \frac{\partial p_j}{\partial p_k} - \frac{\partial q_i}{\partial p_k} \frac{\partial p_j}{\partial q_k} \right) = \delta_{ij} \qquad (A2.9)$$

where δ_{ij} is Kronecker's delta and is equal to zero except for $i=j$ when it is equal to unity. These expressions should be compared with (3.69)–(3.71) derived in chapter 3. In fact, comparing (3.75) and (A2.1) we find that

$$[u, H] = -\frac{j}{\hbar} \langle [\hat{u}, \hat{H}] \rangle \qquad (A2.10)$$

In general, Poisson's brackets go over into the commutators of quantum mechanics as indicated by (A2.10).[2]

References

1. H. Goldstein, op. cit.; Sections 7.3 and 8.5.
2. L. I. Schiff, op. cit.; Section 23, p. 133 *et seq.*

Appendix 3. Probability

For the convenience of those readers who are not very familiar with problems involving probability considerations, a brief summary of the relevant concepts and ideas is given here, a more detailed discussion being available elsewhere.[1]

1. Continuous distributions; a single random variable

The probability that the random variable ξ should have its value in the interval $(x, x+dx)$ is given by

$$Pr\{x < \xi \leqslant x+dx\} = f(x)\,dx \qquad (A3.1)$$

where $f(x)$ is called the probability density (or frequency) function. The related probability of finding the random variable $\xi \leqslant x$ is given by

$$Pr\{\xi \leqslant x\} = \int_{-\infty}^{x} f(x)\,dx = F(x) \qquad (A3.2)$$

where $F(x)$ is called the distribution function. By definition, $f(x)$ must be continuous, single valued and positive everywhere. Also, since the random variable must have some value in the interval $(-\infty, +\infty)$, we have

$$\int_{-\infty}^{+\infty} f(x)\,dx = 1 \qquad (A3.3)$$

The mean or expectation value of the random variable ξ with respect to $f(x)$ is given by

$$E(\xi) = \langle \xi \rangle = \alpha_1 = \int_{-\infty}^{+\infty} xf(x)\,dx \qquad (A3.4)$$

α_1 is also called the first moment of the distribution. The higher moments are defined by

$$E(\xi^{\nu}) = \langle \xi^{\nu} \rangle = \alpha_{\nu} = \int_{-\infty}^{+\infty} x^{\nu}f(x)\,dx \qquad (A3.5)$$

Moments about the mean or the so-called central moments are given by

$$E\{(\xi-\langle\xi\rangle)^{\nu}\} = \langle(\xi-\langle\xi\rangle)^{\nu}\rangle = \mu_{\nu} = \int_{-\infty}^{+\infty} (x-\langle\xi\rangle)^{\nu}f(x)\,dx \quad (A3.6)$$

The most important of them is the variance since it is closely related to the actual spread of the distribution

$$D^2(\xi) = \sigma^2 = E\{(\xi - \langle\xi\rangle)^2\} = \mu_2 = \int_{-\infty}^{+\infty} (x - \langle\xi\rangle)^2 f(x) \, dx$$

$$= \langle x^2 \rangle - \langle x \rangle^2 \qquad (A3.7)$$

where σ is called the standard deviation.

2. Continuous distributions; two random variables

In the case of two random variables we have the joint probability

$$Pr\{x < \xi \leqslant x + dx, y < \eta \leqslant y + dy\} = f(x, y) \, dx \, dy \qquad (A3.8)$$

and the joint distribution function

$$Pr\{\xi \leqslant x, \eta \leqslant y\} = \int_{-\infty}^{x} \int_{-\infty}^{y} f(x, y) \, dx \, dy = F(x, y) \qquad (A3.9)$$

so that

$$f(x, y) = \frac{\partial^2 F}{\partial x \, \partial y} \qquad (A3.10)$$

and

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x, y) \, dx \, dy = 1 \qquad (A3.11)$$

We can now form two marginal probability density functions,

$$f_1(x) = \int_{-\infty}^{+\infty} f(x, y) \, dy \qquad (A3.12)$$

$$f_2(y) = \int_{-\infty}^{+\infty} f(x, y) \, dx \qquad (A3.13)$$

which define the respective probability of the random variables $x < \xi \leqslant x + dx$ or $y < \eta \leqslant y + dy$, whatever the value of the other random variable. If the random variables ξ and η are quite independent then, by definition, the joint probability density function is given by

$$f(x, y) = f_1(x) f_2(y) \qquad (A3.14)$$

The ordinary and central moments of the distribution are now defined by

$$\alpha_{ik} = E(\xi^i \eta^k) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} x^i y^k f(x, y) \, dx \, dy \qquad (A3.15)$$

$$\mu_{ik} = E\{(\xi - \alpha_{10})^i(\eta - \alpha_{01})^k\}$$

$$= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (x - \alpha_{10})^i(y - \alpha_{01})^k f(x, y) \, dx \, dy \quad \text{(A3.16)}$$

By definition

$$\mu_{10} = \mu_{01} = 0, \quad \mu_{20} = \alpha_{20} - \alpha_{10}^2 = \sigma_1^2 \quad \text{variance of } \xi$$

$$\mu_{11} = \alpha_{11} - \alpha_{10}\alpha_{01} \quad \text{covariance of } \xi \text{ and } \eta$$

$$\mu_{02} = \alpha_{02} - \alpha_{01}^2 = \sigma_2^2 \quad \text{variance of } \eta \quad \text{(A3.17)}$$

where σ_1 and σ_2 are respectively the standard deviations of the marginal distributions (A3.12) and (A3.13). If ξ and η are independent

$$\alpha_{ik} = \alpha_{i0}\alpha_{0k}$$

$$\mu_{ik} = \mu_{i0}\mu_{0k}$$

$$\mu_{11} = \mu_{10}\mu_{01} = 0 \quad \text{(A3.18)}$$

The ratio

$$\rho = \frac{\mu_{11}}{(\mu_{20}\mu_{02})^{\frac{1}{2}}} = \frac{\mu_{11}}{\sigma_1\sigma_2} \quad \text{(A3.19)}$$

is called the correlation coefficient and is zero when ξ and η are independent.

3. Discrete distributions; a single random variable

In the case of discrete distributions, we have to substitute summation for integration whenever appropriate or, if preferred, use the more advanced concept of the Lebesgue–Stjeltjes integration.[2]

If the probability of the random variable ξ to have a certain discrete value x_n is

$$Pr\{\xi = x_n\} = p_n \quad \text{(A3.20)}$$

then the probability that $\xi \leqslant x$ is

$$Pr\{\xi \leqslant x\} = \sum_{\substack{n \\ x_n \leqslant x}} p_n \quad \text{(A3.21)}$$

As in the case of continuous distributions, we must have

$$\sum_n p_n = 1 \quad \text{(A3.22)}$$

where the summation is taken over all the values of n, since the random variable ξ must assume one of the prescribed values x_n.

The ordinary and central moments of the distribution are now given by

$$E(\xi^\nu) = \langle \xi^\nu \rangle = \alpha_\nu = \sum_n x_n^\nu p_n \tag{A3.23}$$

$$E\{(\xi - \langle \xi \rangle)^\nu\} = \langle (\xi - \langle \xi \rangle)^\nu \rangle = \mu_\nu = \sum_n (x_n - \langle \xi \rangle)^\nu p_n \tag{A3.24}$$

Again, the variance is defined as

$$D^2(\xi) = \sigma^2 = E\{(\xi - \langle \xi \rangle)^2\} = \mu_2 = \sum_n (x_n - \langle \xi \rangle)^2 p_n$$

$$= \langle x^2 \rangle - \langle x \rangle^2 \tag{A3.25}$$

where σ is the standard deviation.

4. Discrete distributions; two random variables

In the case of two random variables, ξ and η, we obtain

$$Pr\{\xi = x_m, \eta = y_n\} = p_{mn} \tag{A3.26}$$

and

$$Pr\{\xi \leqslant x, \eta \leqslant y\} = \sum_{\substack{m \\ x_m \leqslant x}} \sum_{\substack{n \\ y_n \leqslant y}} p_{mn} \tag{A3.27}$$

Again

$$\sum_m \sum_n p_{mn} = 1 \tag{A3.28}$$

where the double summation extends over all m and n.

The two marginal distributions are now respectively given by

$$p_m = \sum_n p_{mn} \tag{A3.29}$$

$$p_n = \sum_m p_{mn} \tag{A3.30}$$

Again, when ξ and η are independent, we obtain

$$p_{mn} = p_m p_n \tag{A3.31}$$

Finally, the two groups of moments of the distribution are now given by

$$\alpha_{ik} = E(\xi^i \eta^k) = \sum_m \sum_n x^i y^k p_{mn} \tag{A3.32}$$

$$\mu_{ik} = E\{(\xi - \alpha_{10})^i (\eta - \alpha_{01})^k\} = \sum_m \sum_n (x - \alpha_{10})^i (y - \alpha_{01})^k p_{mn} \tag{A3.33}$$

the relationships (A3.17)–(A3.19) being equally valid for continuous and discrete distributions.

It should be noted that all the definitions quoted here can be extended

to cover more than two random variables, in particular, they can be applied in the case of three random variables, a situation which often arises in quantum mechanics when three-dimensional systems are being considered.

References

1. W. Feller, op. cit. H. Cramer, *Mathematical methods of statistics*, Princeton University Press, Princeton, N.J., 1946.
2. H. Cramer, op. cit.

Appendix 4.
Reduced Mass of the Electron in the Hydrogen Atom

Consider the time-independent Hamiltonian of a system comprising two particles

$$H = E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2) \tag{A4.1}$$

Since such a system must be conservative, its Hamiltonian is equal to the total energy, which in turn is given by the sum of the kinetic energies of the two particles taken separately and the potential energy V, where V depends on the six position variables through the respective position vectors of the two particles $\mathbf{r}_1 = (x_1, y_1, z_1)$ and $\mathbf{r}_2 = (x_2, y_2, z_2)$. If we now treat all quantities appearing in (A4.1) as operators, we obtain Schrödinger's wave equation valid for a system of two particles

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2 \Psi}{\partial x_1^2} + \frac{\partial^2 \Psi}{\partial y_1^2} + \frac{\partial^2 \Psi}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2 \Psi}{\partial x_2^2} + \frac{\partial^2 \Psi}{\partial y_2^2} + \frac{\partial^2 \Psi}{\partial z_2^2}\right)$$

$$+ V(\mathbf{r}_1, \mathbf{r}_2) = j\hbar\frac{\partial \Psi}{\partial t} \tag{A4.2}$$

where $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, t)$, must be a function of the six position variables of the two particles and of time (see chapter 8). Since we are considering a conservative system, both the Hamiltonian and the potential function V must be time independent; we can thus separate the variables, following (4.13), and write

$$\Psi = \psi(\mathbf{r}_1, \mathbf{r}_2)\, e^{-jEt/\hbar} \tag{A4.3}$$

Substituting this in (A4.2) we obtain an expression for the time-independent Schrödinger equation of the system of two particles

$$\frac{\hbar^2}{2m_1}\left(\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2}\right) + \frac{\hbar^2}{2m_2}\left(\frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial y_2^2} + \frac{\partial^2 \psi}{\partial z_2^2}\right)$$

$$+ \{E - V(\mathbf{r}_1, \mathbf{r}_2)\}\psi = 0 \tag{A4.4}$$

Note that the position of the mass centre of two particles m_1 and m_2 is given by

$$\mathbf{r}_0 = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{A4.5}$$

where the position vector $\mathbf{r}_0 = (x_0, y_0, z_0)$. Using the same notation, we define the distance between the particles as

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \tag{A4.6}$$

where $\mathbf{r} = (x, y, z)$.

It is now necessary to change the independent variables in (A4.4) from $(\mathbf{r}_1, \mathbf{r}_2)$ to $(\mathbf{r}_0, \mathbf{r})$. Bearing in mind that, in general, for a function $\psi(x_1, \ldots) = \psi\{x_1(x_0, x), \ldots\}$,

$$\frac{\partial^2\psi}{\partial x_1^2} = \frac{\partial^2\psi}{\partial x_0^2}\left(\frac{\partial x_0}{\partial x_1}\right)^2 + \frac{\partial^2\psi}{\partial x^2}\left(\frac{\partial x}{\partial x_1}\right)^2 + 2\frac{\partial^2\psi}{\partial x_0 \partial x}\frac{\partial x_0}{\partial x_1}\frac{\partial x}{\partial x_1}$$
$$+ \frac{\partial\psi}{\partial x_0}\frac{\partial^2 x_0}{\partial x_1^2} + \frac{\partial\psi}{\partial x}\frac{\partial^2 x}{\partial x_1^2} \tag{A4.7}$$

we obtain, substituting from (A4.5) and (A4.6)

$$\frac{\partial^2\psi}{\partial x_1^2} = \frac{\partial^2\psi}{\partial x_0^2}\left(\frac{m_1}{m_1 + m_2}\right)^2 + \frac{\partial^2\psi}{\partial x^2} - 2\frac{\partial^2\psi}{\partial x_0 \partial x}\frac{m_1}{m_1 + m_2} \tag{A4.8}$$

Carrying out similar operations for the remaining five variables y_1, z_1, x_2, y_2, z_2 and substituting in (A4.4) we find that

$$\frac{\hbar^2}{2M}\left(\frac{\partial^2\psi}{\partial x_0^2} + \frac{\partial^2\psi}{\partial y_0^2} + \frac{\partial^2\psi}{\partial z_0^2}\right) + \frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \{E - V\}\psi = 0 \tag{A4.9}$$

where

$$M = m_1 + m_2 \tag{A4.10}$$

is the total mass of the system and

$$m = \frac{m_1 m_2}{m_1 + m_2} \tag{A4.11}$$

is the so-called reduced mass.

We can now use the following argument; if our system represents an electrically neutral atom, such as a hydrogen atom which is enclosed in a box with perfectly elastic walls, then experiments show that the movement of the atom as a whole is independent of the relative positions of the particles within the atom. (An excellent discussion of this so-called 'quantum ladder' effect is given elsewhere.[1]) Thus the potential function V in (A4.9) must be the sum of two terms, one depending on the position of the centre of gravity of the atom, $\mathbf{r}_0$, and the other depending on the

distance between the two particles, $\mathbf{r}$, giving

$$V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_0) + V(\mathbf{r}) \tag{A4.12}$$

Similarly, since the position of the atom within the box is independent of the relative position of its component particles, the probability of finding particle m_1 at $\mathbf{r}_1$ and particle m_2 at $\mathbf{r}_2$ must have the form of a product of two functions, one depending on $\mathbf{r}_0$ and the other on $\mathbf{r}$ only,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_0, \mathbf{r}) = \psi(\mathbf{r}_0)\psi(\mathbf{r}) \tag{A4.13}$$

Substituting (A4.10)–(A4.13) in (A4.9) we can split it now into two separate equations

$$\frac{\hbar^2}{2M}\left(\frac{\partial^2\psi_0}{\partial x_0^2} + \frac{\partial^2\psi_0}{\partial y_0^2} + \frac{\partial^2\psi_0}{\partial z_0^2}\right) + \{E^M - V(\mathbf{r}_0)\}\psi_0 = 0 \tag{A4.14}$$

and

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \{E^m - V(\mathbf{r})\}\psi = 0 \tag{A4.15}$$

where

$$E = E^M + E^m \tag{A4.16}$$

Thus the problem of solving (A4.9) which has six independent variables, has now been reduced to that of solving two equations, (A4.14) and (A4.15), each containing three variables only. The solution of these equations will give us two sets of eigenvalues, one set, E_n^M, referring to the eigenvalues of the system as a whole and the other set, E_n^m, referring to the eigenvalues associated with the energy levels of the particles within the atom. The two sets of eigenvalues give us a doubly infinite series representing all the possible eigenvalues of the total energy of the system. Expressing the operator ∇^2 in (A4.15) in terms of polar spherical coordinates (r, θ, ϕ) and bearing in mind the fact that for a Coulomb field of force $V(\mathbf{r}) = V(r)$ where r is the distance between the two particles, we find that (A4.15) and (4.63) are identical, except that now in place of the mass of an electron $m = m_1$ we have the reduced mass $m = m_1 m_2/(m_1 + m_2)$. In the case of the hydrogen atom this becomes equal to $m = (1836/1837)m_e = 0.9995 m_e$, where $m_e = 9.11 \times 10^{-31}$ kg.

Reference

1. V. Weisskopf, The quantum ladder, *International Science and Technology* No. 18: 62–70, June, 1963.

Appendix 5.
Boltzmann's Statistics

Let us describe the state of a system comprising a large number of identical particles by specifying a distribution function $n_i = N_i/\tau_i$, where N_i is the number of particles in an element of phase space[1] τ_i; in cartesian coordinates $\tau_i = \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{v} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$ (here we treat the position $\mathbf{r}$ and velocity $\mathbf{v}$ of the particle as two independent variables). In principle, we could measure n_i by counting the number of particles N_i in each cell τ_i, i.e., the number of particles situated in an element of volume $\mathrm{d}\mathbf{r}$ centred on $\mathbf{r}$ *and* having velocities in the interval $\mathrm{d}\mathbf{v}$ centred on $\mathbf{v}$; in the limit, n_i is assumed to approach the phase-space density function $n(\mathbf{r}, \mathbf{v})$ which is continuous.

We can now label each particle with the number i of the cell to which it belongs, particles in the same cell having the same label, i.e., the same $\mathbf{r}$ and $\mathbf{v}$ and thus being indistinguishable. It is clear that a given distribution n_i can be realized by many different arrangements of distinguishable
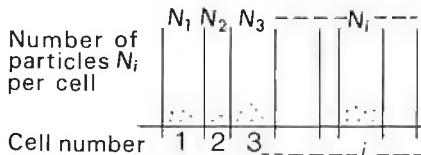
Fig. A5.1. Particle distribution in classical mechanics.

particles. For example, we can interchange the cells and labels of two particles A and B without affecting the function n_i in any way. (We are not interested here in rearrangements of indistinguishable particles, i.e., of particles belonging to the same cell τ_i, because we would not know how to observe it.)

We now measure the likelihood of occurrence of a given distribution n_i by the number of ways the distinguishable particles can be rearranged without altering it. If the cells τ_i are all of equal size, each particle has the same likelihood of finding itself in any one of them (equal *a priori* probability); also, for non-interacting particles, this likelihood cannot be dependent on the presence of other particles in the cell. Assume that the total number of particles in the system is $N = \sum_i N_i$. If there is only one

particle in each cell, then the total number of possible rearrangements of distinguishable particles, i.e., the corresponding number of permutations is simply $N!$; if there are N_i particles in the ith cell, $N_i!$ of these permutations do not count and taking all cells into account we are left with a total number of permutations given by

$$W = \frac{N!}{N_1! N_2! \ldots N_i! \ldots}$$

$$= \frac{N!}{\prod_i N_i!} \tag{A5.1}$$

However, in practice, the assumption that all cells are of the same size is too restrictive and we must consider what happens when the cells differ in size. If one cell is twice as large as the others, the likelihood of a particle falling into it is doubled, the likelihood of two particles falling into it is quadrupled and so on (the likelihood of a joint event is obtained by multiplying the likelihoods of the two constituent events assuming that they are independent, see (A3.31)). Thus, if the size of the cell is τ_i, the likelihood of N_i particles being in it is given by $\tau_i^{N_i}$. Since the same must apply to all cells, we multiply (A5.1) by $\tau_1^{N_1} \tau_2^{N_2} \cdots \tau_i^{N_i} \cdots$ to obtain

$$W = \frac{N! \prod_i \tau_i^{N_i}}{\prod_i N_i!} \tag{A5.2}$$

different cells now having unequal *a priori* probabilities (weights). (An alternative derivation of (A5.2) can be found elsewhere.)[2] We can now employ a useful approximation for the factorial which is valid for large values of the argument.*

$$N! \sim \left(\frac{N}{e}\right)^N \tag{A5.3}$$

where e is the basis of natural logarithms. Substituting (A5.3) in (A5.2) we obtain

$$W = \frac{N^N \prod_i \tau_i^{N_i}}{\prod_i N_i^{N_i}} \tag{A5.4}$$

or, in the logarithmic form which is more convenient for further discussion,

$$\ln W = N \ln N + \sum_i N_i \ln \tau_i - \sum_i N_i \ln N_i$$

$$= N \ln N - \sum_i N_i \ln n_i \tag{A5.5}$$

where, in the second line, the relationship $n_i = N_i / \tau_i$ has been used.

* A more accurate approximation due to Stirling gives $N! \sim (2\pi N)^{\frac{1}{2}} (N/e)^N$.

In order to obtain the most probable distribution n_i, we now have to find the maximum of (A5.5), subject to two constraints, viz., that the total number of particles

$$N = \sum_i N_i = \sum_i n_i \tau_i \qquad (A5.6)$$

and the total energy of the system

$$E = \sum_i E_i N_i = \sum_i E_i n_i \tau_i \qquad (A5.7)$$

remain constant (here E_i is the energy of a particle in cell τ_i). Using the method of Lagrange's multipliers[3] we calculate the differences $\delta(\ln W)$, δN, δE, and equate them to zero; thus from (A5.5)–(A5.7)

$$\delta(\ln W) = -\sum_i \delta(N_i \ln n_i)$$

$$= -\sum_i \delta n_i \tau_i \ln n_i - \sum_i \tau_i \delta n_i = 0 \qquad (A5.8)$$

$$\delta N = \sum_i \delta n_i \tau_i = 0 \qquad (A5.9)$$

$$\delta E = \sum_i E_i \delta n_i \tau_i = 0 \qquad (A5.10)$$

Now multiply (A5.9) by α, (A5.10) by β and subtract both from (A5.8); the new equation must be zero irrespective of the manner in which the phase space τ has been subdivided into cells of unequal size τ_i—thus it must be valid for each i and we obtain

$$\alpha + \beta E_i + 1 + \ln n_i = 0 \qquad (A5.11)$$

or

$$n_i = e^{-\alpha - 1} e^{-\beta E_i} \qquad (A5.12)$$

Substituting (A5.12) in (A5.6) we obtain

$$N = \sum_i n_i \tau_i$$

$$= e^{-\alpha - 1} \sum_i e^{-\beta E_i} \tau_i \qquad (A5.13)$$

which permits the elimination of one of the constants

$$n_i = \frac{N e^{-\beta E_i}}{\sum_i e^{-\beta E_i} \tau_i} \qquad (A5.14)$$

The other constant can only be determined with the help of thermodynamics[4]; we then obtain $\beta = 1/kT$, where T is temperature and k is Boltzmann's constant. Substituting this in (A5.14) and dividing both sides

by N, we finally obtain the function describing the Boltzmann distribution of energy

$$f_i = \frac{1}{\sigma} e^{-E_i/kT} \tag{A5.15}$$

where

$$\sigma = \sum_i e^{-E_i/kT} \tau_i \tag{A5.16}$$

and is the so-called *partition sum*. It should be added here that the summation is over the states i and not over the energies E_i; for continuous distributions the sum becomes a phase-space integral of the form $\iint \ldots d\mathbf{r}\, d\mathbf{v}$ in cartesian coordinates.

In the case of a monatomic gas which is in a state of equilibrium at temperature T, the relevant part of the element of phase space $\tau_i = d\mathbf{r}\, d\mathbf{v}$ is $d\mathbf{v} = dv_x\, dv_y\, dv_z$; since in classical mechanics the energy is assumed to be continuous, we can write $E_i = E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. Substituting in (A5.16) and changing summation to integration we now obtain

$$\sigma = \left(\frac{2\pi kT}{m}\right)^{\frac{3}{2}} \tag{A5.17}$$

From (A5.15) the relevant probability density function is now given by the familiar expression

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-(m^2 kT)(v_x^2 + v_y^2 + v_z^2)} \tag{A5.18}$$

In order to find the probability density function $f(E)$ depending on E alone, we have to convert $f(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z$ from cartesian coordinates (v_x, v_y, v_z) to spherical polar coordinates (v, θ, ϕ), where v is the magnitude of the velocity $\mathbf{v}$, integrate with respect to θ and ϕ and change the variable v to E, using the relationship $E = \frac{1}{2}mv^2$; this gives

$$f(E) = \frac{2}{\pi^{\frac{1}{2}} k^{\frac{3}{2}} T^{\frac{3}{2}}} E^{\frac{1}{2}} e^{-E/kT} \tag{A5.19}$$

as the correct probability density function for the energy E. Here a direct integration of (A5.16) with respect to E would have given an incorrect result because of the implicit reduction in the number of dimensions.

As another example, let us consider the important case of a system comprising a large number of one-dimensional harmonic oscillators. The appropriate element of the phase space is now given by $\tau_i = dz\, dv_z$; bearing in mind that for classical oscillators the energy $E_i = E = \frac{1}{2}\kappa z^2 + \frac{1}{2}mv_z^2$, section 4.5, and is continuous, we integrate (A5.16) with respect to z and v_z and obtain

$$\sigma = \frac{2\pi kT}{\omega_c m} \tag{A5.20}$$

where, as usual, $\omega_c^2 = \kappa/m$. Substituting this in (A5.15) we find that now

$$f(z, v_z) = \frac{\omega_c m}{2\pi kT} e^{-(m/2kT)(\omega_c^2 z^2 + v_z^2)} \tag{A5.21}$$

To obtain the probability density function which depends on E alone we again have to express $f(z, v_z)\, dz\, dv_z$ in polar coordinates (ρ, ϕ), where $\rho^2 = \frac{1}{2}(\kappa z^2 + m v_z^2) = E$, integrate with respect to ϕ and then change from ρ to E; this gives

$$f(E) = \frac{1}{kT} e^{-E/kT} \tag{A5.22}$$

as the correct expression for the probability density function describing the energy distribution among a large number of classical, non-interacting, harmonic oscillators which are in equilibrium at temperature T. Although in this case (A5.22) could have been obtained directly by changing summation to integration in (A5.15) and (A5.16), this is merely a coincidence and does not apply in general, as we have seen in connection with our previous example.

References

1. G. Joos, op. cit.; Chapter XXXIV. A. Sommerfeld, op. cit.; Chapter IV. K. K. Darrow, Memorial to classical statistics, *Bell System Tech. J.* **22**: 108–35 (1943).
2. A. Sommerfeld, op. cit.; Section 29.
3. R. Courant, loc. cit.
4. G. Joos, loc. cit. R. Sommerfeld, op. cit.; Section 30.

Appendix 6.
Bra and Ket Notation

In addition to the Schrödinger notation we have used throughout there is the so-called bra and ket notation due to Dirac.[1] Since this notation is widely used in practice we summarize it briefly.

In section 7.5 we have discussed the basic concepts of the matrix representation of quantum mechanics due to Heisenberg and Dirac. In this connection, Dirac introduced a new notation which not only avoids an excessive use of subscripts and superscripts but also focuses attention on the quantum numbers defining the state of a system, rather than on the algebraic form of the corresponding wave functions. Dirac decided to call the column matrix $[a_i]$ of [7.34] a 'ket' vector and write it as $|\Psi\rangle$, or, in the case of an eigenfunction,

$$|lmn\rangle \equiv \Psi_{lmn} \tag{A6.1}$$

Similarly, the corresponding adjoint row matrix $[a_i]^\dagger = [a_i^*]$ was called a 'bra' vector and written $\langle\Psi|$, or, in the case of an eigenfunction,

$$\langle lmn| \equiv \Psi_{lmn}^* \tag{A6.2}$$

Using this notation, the normalization, (3.18) and [7.35], and the orthogonality conditions, (5.2) and [7.36] for a set of Schrödinger eigenfunctions, become simply

$$\int \Psi_{l'm'n'}^* \Psi_{lmn} \, d\mathbf{r} \equiv \langle l'm'n'|lmn\rangle = \delta_{ll'} \, \delta_{mm'} \, \delta_{nn'} \tag{A6.3}$$

where, as usual, $\delta_{ll'}$, is zero for $l \neq l'$ and unity for $l = l'$, the same applying to the other two functions. This type of notation is particularly helpful if we wish to consider various matrix elements such as, for example, $\overline{H}_{ki}'$ in (7.7) or $\hat{H}_{ki}$ in (7.52), since we can now write, following (A6.3)

$$\int \Psi_k^* \hat{H}' \Psi_i \, d\mathbf{r} \equiv \langle k| \hat{H}' |i\rangle \tag{A6.4}$$

which is much neater and contains all the required information. In fact, (A6.4) explains the origin of Dirac's notation. The angular brackets $\langle \rangle$ which are frequently used to denote the mean or expectation value in the theory of probability and which are closely related to the general concept

of the observables, (3.66), can be imagined to consist of two parts, a 'bra' $\langle\ |$ and a 'ket' $|\ \rangle$. These, when joined together either directly, as in (A6.3) or by an intervening operator, as in (A6.4), neatly provide the majority of the algebraic expressions used in quantum mechanics. In fact, it can be said, in general, that all rules of quantum mechanics based on the Schrödinger formulation are paralleled by corresponding operations based on the matrix formulation and by those using the bras and kets of Dirac's notation. An excellent summary of these ideas, together with further extension of Dirac's notation, can be found elsewhere.[2]

References

1. P. A. M. Dirac, *The principles of quantum mechanics*, 3rd and later editions, Oxford University Press, Oxford, 1947.
2. P. T. Matthews, op. cit.; Chapter 12.

Useful Constants*

$h = 6.625 \times 10^{-34}$ J.s   Planck's constant
$\quad = 4.135 \times 10^{-15}$ eV.s

$\hbar = 1.054 \times 10^{-34}$ J.s $h/2\pi$
$\quad = 6.582 \times 10^{-16}$ eV.s

$k = 1.380 \times 10^{-23}$ J/°K   Boltzmann's constant
$\quad = 8.617 \times 10^{-5}$ eV/°K

$1/k = 11,605$ °K/eV

$c = 299,793 \times 10^{3}$ m/s   velocity of light (vacuum)

$e = 1.602 \times 10^{-19}$ C   electron charge
$\quad = (4.806 \times 10^{-10}$ e.s.u.$)$

$m_e = 9.108 \times 10^{-31}$ kg   electron mass

$e/m_e = 1.759 \times 10^{11}$ C/kg   electron charge to mass ratio

$(2e/m_e)^{\frac{1}{2}} = 5.931 \times 10^{5}$ C$^{\frac{1}{2}}$/kg$^{\frac{1}{2}}$

$m_p = 1.672 \times 10^{-27}$ kg   proton mass

$m_n = 1.675 \times 10^{-27}$ kg   neutron mass

$m_p/m_e = 1836$

$\hbar^2/2m_e = 6.103 \times 10^{-39}$ J.m^2
$\quad = 3.810 \times 10^{-20}$ eV.m^2

$a_0 = 0.529 \times 10^{-10}$ m   Bohr radius $\hbar^2 4\pi\varepsilon_0/m_e e^2$ (or $\hbar^2/m_e e^2$ in e.s.u.)

$\mu_B = 9.273 \times 10^{-24}$ A.m^2 Bohr magneton $e\hbar/2m_e$

$Ry = 2.180 \times 10^{-18}$ J   Rydberg constant $\hbar^2/2m_e a_0^2$
$\quad = 13.60$ eV

$R_\infty = 109,737.31$ cm^{-1} Rydberg number Ry/hc

$\varepsilon_0 = 8.854 \times 10^{-12}$ F/m   permittivity of free space

$\mu_0 = 1.257 \times 10^{-6}$ H/m   permeability of free space $4\pi \times 10^{-7}$

1 eV $= 1.602 \times 10^{-19}$ J

1 Tesla $= 1$ Wb/m$^2 = 10^4$ gauss

1 J $= 10^7$ erg

* Based on: E. R. Cohen, Mathematical analysis of the universal physical constants, *Supplemento del Nuovo Cimento* **6**: 110–40 (1957).

Index

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